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Hugo Gallardo, Rodrigo Cristiano, Juliana Eccher, Ivan Helmuth Bechtold, Catarina N Tironi, André A Vieira, and Fernando Molin Langmuir, Just Accepted Manuscript • DOI: 10.1021/la3020139 • Publication Date (Web): 02 Jul 2012 Downloaded from http://pubs.acs.org on July 4, 2012

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Graphical Abstract 41x21mm (300 x 300 DPI)

# Luminescent Columnar Liquid Crystals Based on Tristriazolotriazine

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ABSTRACT: Five discotic molecules comprised of a tris[1,2,4]triazolo[1,3,5] triazine core were designed and synthesized to obtain luminescent and charge-transporting columnar liquid crystalline materials. With the exception of one compound, containing terminal hydroxyl groups, all compounds presented a wide-thermal-range and stable columnar liquid crystalline phase, characterized by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction (XRD) techniques. The phase formation appeared to be associated to some extent with interdigitation of the alkoxy and benzylalkoxy portion, as suggested by the XRD results. All compounds have a strong blue luminescence in solution and solid phase. At the temperature at which the compounds enter in the mesophase the luminescence decreases significantly. This

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result suggests that entrance into the Col<sub>h</sub> phase is accompanied by a better  $\pi$ -stacking of the peripheral phenyl rings compared to the solid phase, consistent with the intramolecular distances (3.5 Å) observed in the XRD analysis. These compounds based on tristriazolotriazine are quite robust with good optical and thermal properties for application as solid state emitters and we anticipate that they may provide an interesting alternative to other discotic molecules based on *N*-heterocycle, which generally present a high temperature Col<sub>h</sub> phase.

#### **INTRODUCTION**

The search for new cores able to exhibit a high thermal stability, columnar mesomorphism at close to room temperature, and a high tendency to yield oriented monodomains is a subject of great interest in the design of smart materials.<sup>1-3</sup> The interest in discotic liquid crystals (DLCs) is due to the advantageous properties of these materials, such as long-range self-assembling (order), self-healing structural defects, ease of processing, high solubility in organic solvents, and charge-carrier mobility.<sup>4,5</sup> These properties are the key feature of new smart materials for electronic and optoelectronic devices based on organic compounds.

Among the DLCs,  $\pi$ -conjugated *N*-heterocycles are strong candidates to be considered in the synthesis of these materials. They can form efficient  $\pi$ - $\pi$  columnar stacks which result in onedimensional (1D) high charge-carrier mobilities (up to 0.1–1.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>6-8</sup> The magnitude of the mobilities is fundamentally determined by the degree of order and  $\pi$ - $\pi$  molecular orbital overlap within the columnar stacks.<sup>9,10</sup> Moreover, disc-like molecules with a  $\pi$ -conjugated *N*-heterocycle are easily functionalized to present columnar mesomorphism. The insertion of simple peripheral aliphatic chains may lead to columnar phases and highly ordered structures with exciting properties from both the scientific and technological points of view.<sup>11</sup> Over recent

decades new discotic liquid crystals have been reported with a large number of  $\pi$ -conjugated Nheterocycle cores such as triazine,<sup>12-14</sup> hexaazatriphenylene,<sup>15</sup> cyclotriphosphacene,<sup>16</sup> triindole,<sup>17</sup> phthalocyanine,<sup>20-22</sup> hexaazatrinaphthylene,<sup>23,24</sup> tricycloquinazoline.<sup>18,19</sup> porphyrin,<sup>25,26</sup> pervlenediimide,<sup>27</sup> and dodecaazatrianthracene.<sup>28</sup> These cores have been exploited in ion transport<sup>29-31</sup> and charges,<sup>32-35</sup> catalysis,<sup>36</sup> and electro-optical applications.<sup>37-40</sup> All of the properties of the DLCs can be controlled by their molecular self-organization processes. Thus, it is important to understand the structure-property relationships on the molecular level. This can be studied through slightly modifying the molecule (e.g. varying the length, volume and functionality of the aliphatic chains) and observing the effect on the DLC properties. In this context, we previously reported the synthesis and chemical characterization of new tris[1,2,4]triazolo[1,3,5] triazines, of which compound 1 exhibited a large stable hexagonal columnar mesophase.<sup>41</sup> Herein, we report the results of our further investigation<sup>42</sup> of this heterocycle as a core in discotic liquid crystal compounds and the study of the mesomorphic behavior, luminescence and conductive capabilities in the solid phase and mesophase range of these compounds. Tristriazolotriazine<sup>43</sup> was found to represent an attractive and interesting alternative to other N-heterocycle cores reported thus far. It was observed to be quite efficient as a core for wide-thermal-range Col<sub>b</sub> phase, blue luminescence and stable thin films.

## EXPERIMENTAL SECTION

**Materials.** All the chemicals were purchased from Aldrich, Acros or Vetec. Toluene, tetrahydrofuran (THF) and  $Et_2O$  were distilled over Na/benzophenone. CHCl<sub>3</sub> was purified by refluxing over CaH<sub>2</sub> followed by distillation. If not specified otherwise, the other solvents were deoxygenated by bubbling with N<sub>2</sub> for 1 h prior to use.

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Measurements and Characterization. <sup>1</sup>H and <sup>13</sup>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 in KBr discs or films. Mass spectra were recorded on Bruker Autoflex III Smartbean with MALDI-TOF techniques, using  $\alpha$ -cyano-4-hydroxycinnamic acid as matrix and high resolution mass spectra were recorded on Bruker micrOTOF-Q II APCI-Qq-TOF mass spectrometer. The textures of the mesophases were determined 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 DSC measurements carried out using TA equipment Q2000 module. TGA measurements were carried out using Shimadzu equipment with a TGA-50 module. Elemental analysis was carried out using a Carlo Erba model E-1110 instrument.

**X-ray Diffraction (XRD) Experiments.** We used the X'PERT-PRO (PANalytical) diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å), the applied power was 1.2 kVA and the scans performed in continuous mode from 2° to 30° (2 $\theta$  angle). The samples consisted of an amount of powder on a glass plate placed in the diffractometer chamber on the TCU2000 temperature control unit (Anton Paar), allowing the temperature control during the measurement. The samples were first heated until the isotropic phase and the diffraction patterns collected during cooling back through the mesophases. As a result, we obtained films of approximately 1 mm thickness.

Absorbance and Fluorescence Measurements. An HP UV-Vis model 8453 spectrophotometer was used to record the absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500. The relative quantum yields of fluorescence ( $\Phi_{Fl}$ ) were determined according to a published method.<sup>44</sup> The absorption and fluorescence measurements in solid state

(thin films) were carried out with the OceanOptics USB4000 spectrophotometer. The absorption was performed on spin-coated films of the compounds on glass substrates (further details available in Ref. 45). To determine the fluorescence as a function of the temperature, the same procedure applied to the XRD samples was adopted. The samples were placed on a hot stage, illuminated with a UV lamp and the emission captured with an optic fiber close to the film. The angular position was chosen so as to avoid the direct incidence and the specular reflection (from the glass plate) of the lamp.

**Circular Dichroism (CD)**. CD spectra were recorded in a Jasco J-810. Neat samples were prepared by casting a tetrahydrofuran solution of the material, at 2 wt %, onto a quartz plate and subsequent melting above the clearing point. As the heating stage, a Mettler FP82, with a central processor Mettler FP80, was used appropriately modified for fixing within the sample holder of the CD spectrometer.

Atomic Force Microscopy (AFM). AFM was performed on the same spin-coated films used for the absorption characterization. We used the model EasyScan2 (Nanosurf) in tapping mode with a scanning rate of 1.0 Hz and 512 x 512 lines. To obtain the film thickness, part of the film was removed with a needle in order to create a step between the film and the substrate.<sup>46</sup>

**Conductivity Measurements**. Conductivity was obtained from a.c. impedance measurements using the an Autolab Electrochemical Instruments conductivity meter, over the frequency range of  $0.1-10^6$  Hz. Cells were prepared using ITO-coated glass plates separated by spacers of 9.0  $\mu$ m. The compounds were inserted by capillarity action using a hot stage, by heating the material until the isotropic phase was achieved, followed by cooling at a rate of 5 °C/min until the mesophase was obtained for the measurement. This procedure is commonly used to generate

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homeotropic alignment and thus the conductivity is measured in the direction of the column organization.

**Synthesis**. The tristriazolotriazines 1-5 were prepared according to previously published procedures.<sup>41</sup> For more detail see support information.

## **RESULTS AND DISCUSSION**

**Synthesis and Characterization of the Materials.** The disc-like molecules **1-5** based on a tristriazolotriazine core were synthesized according to our previous methodology<sup>41</sup> by reacting three equivalents of the respective aryltetrazole with cyanuric chloride in the presence of potassium carbonate (Scheme 1). Our design strategy was to modify the peripheral region of the disc-like molecule in order to investigate the influence of a larger volume and different functionality (chirality and the presence of OH groups) on the columnar arrangement. The chemical structures were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and MALDI-MS. In our previous work we have entirely elucidated the regiochemistry of the three triazole ring obtained from this reaction, including the X-ray structure and <sup>15</sup>N NMR of the tris[1,2,4]triazolo[1,3,5]triazine ring.





Scheme I. Synthesis of the discotic liquid crystals based on tris[1,2,4]triazolo[1,3,5]triazines. Compound **3** is a diastereomeric mixture

**Liquid Crystalline Properties**. The thermotropic liquid crystalline properties of compounds **1-5** are summarized in Table 1. With regard to the thermal characteristics, all molecules presented good stability, measured by TGA under a nitrogen atmosphere, with decomposition temperatures above 400 °C. An exception was compound **5**, with more labile benzyl groups, for which the onset of decomposition was at 315 °C. With the exception of compound **4**, containing the terminal hydroxyl groups, all other compounds presented columnar liquid crystalline phases, characterized by Differential Scanning Calorimetry (DSC), Polarized Optical Microscopy (POM) and X-ray diffraction (XRD).

Compound	$\mathbf{D}$	XRD data	XRD data		
Compound.	Phase transition profile	T (°C)	<i>a</i> <sup><i>b</i></sup> (Å)		
1	Cr 92.2 (19.3) Col <sub>h</sub> 207.6 (6.8) I	150	20.4		
	I 203.3 (5.8) Col <sub>h</sub> 91.1 (19.6) Cr	130	30.4		
2	Cr 41.7 (8.6) Col <sub>h</sub> 166.6 (4.1) I	150	26.2		
	I 164.0 Col <sup>c</sup> 159.2 Col <sub>h</sub> (4.4) 31.7 (5.4) Cr	150	26.3		
2	Col <sub>h</sub> 158.3 (2.8) I	1.50	24.1		
3	I 157.4 (2.4) Col <sub>h</sub> <sup>d</sup>	150			
4	Cr 111.3 (46.5 ) I				
	I 100.9 (52.9) Cr				
5	Cr 174.4 (10.8) Col <sub>h</sub> 264.1 <sup>e</sup> (6.4) I		38.1		
	I 252.2 (3.0) Col <sub>b</sub> 153.8 (6.8) Cr	200			

<sup>*a*</sup>Transition temperatures (°C) and in parentheses the transition enthalpies (kJ/mol), determined by DSC during heating (first line) and cooling (second line) cycles. Cr = crystalline;  $Col_h =$ hexagonal columnar; I = isotropic liquid. <sup>*b*</sup>Lattice parameters for the hexagonal lattice. <sup>*c*</sup>Overlapped with the Col-Col<sub>h</sub> phase transition; <sup>*d*</sup>No crystallization observed at room temperature (20 °C). <sup>*e*</sup>Some extent of thermal decomposition observed, especially when paused for a long time at this temperature

For all DLC compounds observed under a polarizing optical microscope, on cooling from the isotropic phase a fan-like texture appears which is characteristic of a hexagonal columnar phase  $(Col_h)$  (Figure 1). On slower cooling (1 °C/min) the dendritic growth typical of a  $Col_h$  phase can be easily observed. Compound **2** contains a chiral center in each terminal chain that is known to cause a helical stacking in the LC columnar assemblies.<sup>47</sup>



Figure 1 Polarized optical photomicrographs (100x) of fan-like textures of  $Col_h$  obtained on cooling of: a) compound 2 at 100 °C; b) compound 3 at 140 °C; c) compound 5 at 170 °C; and d) compound 5 at 142 °C.

On cooling compound **2** from an isotropic liquid, the DSC measurements showed two overlapped transitions, indicating that it passes through a different columnar arrangement before entering the  $Col_h$  phase (Table 1). Interestingly, there was no apparent difference in the optical texture even on bringing the compound very slowly from the isotropic liquid. Due to the very narrow temperature ranges within which these transitions occur, they could not be properly characterized by XRD.

Compared to compound 1, which contains straight 12 C alkyl chains, compounds 2 and 3 with branched and shorter peripheral units showed lower isotropization temperatures, and exhibited lower melting points. Compound 2, for instance, exhibited a columnar LC phase upon heating at above 41 °C and compound 3 showed the Col<sub>h</sub> phase at room temperature. The lower values for

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the transition enthalpies ( $\Delta H = 2 - 4 \text{ kJ/mol}$ ) for the transition from the Col<sub>h</sub> to the isotropic phase compared to the other studied compounds ( $\Delta H = 6 - 7 \text{ kJ/mol}$ ) provide evidence of weakened intermolecular  $\pi$ - $\pi$  interactions associated with the core in these molecules, which may result in an isotropic liquid phase at lower temperatures. Due to the presence of the benzyl groups in **5**, this compound has a higher melting point (174 °C) along with a higher isotropization temperature (264 °C). On cooling compound **5**, as observed by POM, the transition from the Col<sub>h</sub> to the crystalline phase is accompanied by a sudden color change from green to reddish, with no other visible changes in the LC texture (see Figures 1c and 1d). Also, according to the POM analysis, some decomposition of compound **5** occurs when the isotropization temperature is reached. The DSC measurements showed no reversibility in the transition temperatures after the second scan, providing further evidence for decomposition of the material.

To confirm the columnar LC structures, XRD measurements were performed for all compounds (Table 1). As in the case of compound **1**, reported in our previous communication, the other compounds also exhibited diffractograms with profiles typical of a hexagonal columnar structure. A representative XRD pattern for **5** in the Col<sub>h</sub> phase at 200 °C is shown in Figure 2. This shows an intense peak in the small-angle region at 33.0 Å, and two very weak peaks at 19.5 and 17.0 with a reciprocal *d*-spacing ratio of  $1 : 3^{1/2} : 2$ , being indexed as (10), (11), and (20) reflections of a two-dimensional hexagonal lattice. In the wide angle region, a diffuse peak at 4.6 Å relative to the peripheral alkoxybenzyl groups is observed. The intercolumnar distances obtained from the XRD analysis are in agreement with the relative sizes of the molecules, diminishing from 30.4 Å in compound **1**, containing the straight alkyl chains with twelve C atoms, to 26.3 Å, 24.1 Å and 38.1 Å in compounds **2**, **3** and **5** respectively. Although the relative

sizes are in agreement with the values found for intercolumnar distances, the measured values are lower than the estimated molecular diameter for all compounds (43, 36, 29, and 50 Å for 1, 2, **3** and **5**, respectively). This could be related to many factors as the interdigitation of the outer chains between neighboring columns, nonlinear conformations of the chains and accommodation of the disordered chains inside the intracolumnar spaces.<sup>48</sup> On cooling from Col<sub>b</sub>, the crystallization occurs with retention of the phase texture observed by POM. The XRD pattern for 5 at 100 °C gave a profile similar to that obtained in the  $Col_h$ , which differ from each other in terms of the dimension of the lattice parameter, this being larger for the lower temperature. To confirm whether interdigitation of the outer chains between neighboring columns is crucial for this tristriazolotriazine core to achieve a columnar LC phase, we designed a molecule containing a hydrogen bonding group (OH group) in the end of the aliphatic chains, compound 4. Indeed, compound 4 did not show an LC phase, although a glassy state with a fan-shaped texture after two heating/cooling cycles could be observed by POM. Although the POM analysis alone was not sufficient to fully discard the presence of a columnar phase, the DSC measurements clearly revealed only a crystalline to isotropic phase transition, with a large transition enthalpy (around 50 kJ/mol). In addition, the XRD analysis of compound 4 showed a crystalline profile, although some similarities with columnar packing were noted, as also seen by POM. The results for the POM and XRD measurements imply a much more organized columnar structure in compound 4, and we believe that this is due to the hydrogen bonding between the terminal OH groups, which prevents interdigitation of the chains. This process may destroy the Col<sub>h</sub> formation, in comparison with compound 1 which is of similar length and volume.



Figure 2 XRD pattern of compound 5 in the Col<sub>h</sub> phase at 200 °C.

**Optical properties**. UV absorption and photoluminescence in  $CH_2Cl_2$  solution, in films and in the  $Col_h$  phase, were performed and the results are summarized in the Table 2. The lowest energy band of the tristriazolotriazine core presented maximum absorption wavelengths for compounds **1-5** in solution at around 308-311 nm. For the spin-coated films the maximum wavelengths had small blue-shifts compared to those in solution (305-309 nm). Very thin films (spin coated or vacuum deposited) may shift the emission toward the blue region<sup>49</sup>.

These bands showed high molar absorption coefficients ( $\varepsilon \sim 20000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), attributed to the  $\pi$ - $\pi$ \* transitions in the heteroaromatic portion of the molecules. Compounds **1-5** exhibited blue fluorescence in solution peaking at around 386 and 389 nm with good quantum yields (41-49%). These compounds are good emitters in solid state. Spin-coated thin films showed intense blue photoluminescence, their spectra become broader compared to that in solution, which indicates the occurrence of intermolecular electronic interactions. The appearance of shoulders in the emission spectra at different intensities led to migration of the maximum wavelength, in most

cases, bathochromically compared to those in solution. An exception in this regard was compound **2** which presented a blue shift in the emission maximum wavelength of around 10 nm. Compound **5** had the largest red-shift in the photoluminescence maximum wavelength (around 30 nm) from 388 nm in solution to 416 nm in solid state, with a much broader spectrum.

	UV/vis abs λ <sub>max</sub> /n	orption m	photo	luminescen λ <sub>max</sub> /nm	ce		
Comp.	Solution <sup>[a]</sup>	Film	Solution <sup>[a]</sup>	Film	$\operatorname{Col}_{h}^{[b]}$	$\Phi_{FL}{}^{[c]}$	$E_g\!/eV^{[h]}$
1	311	307	387	391	393	0.47	3.56
2	311	305	388	378 <sup>[d]</sup>	381 <sup>[e]</sup>	0.47	3.52
3	310	308	389	396	396	0.41	3.51
4	311	307	389	397	-	0.44	3.48
5	308	309	386	416 <sup>f</sup>	382 <sup>g</sup>	0.49	3.46

 Table 2 Optical data for compounds 1-5

<sup>a</sup>CH<sub>2</sub>Cl<sub>2</sub> solution (10<sup>-5</sup> M). <sup>b</sup>Taken at a temperature just above the Cr-Col<sub>h</sub> transition. <sup>c</sup>Relative to PBD ( $\Phi_{FI}$ =0.83).<sup>54</sup> <sup>d</sup>Shoulder appeared at 402 nm. <sup>e</sup> Shoulders appeared at 403 and 416 nm. <sup>f</sup>Shoulders appeared at 377 and 478 nm. <sup>g</sup>Very weak emission. <sup>h</sup>Determined from absorption spectra of the films.

Photoluminescence was measured in the condensed LC state. On heating the samples from room temperature, several spectra were taken for each of the LC compounds in the crystal, liquid crystal and isotropic phases (Figure 3a). In general, the maximum wavelength did not vary significantly from that obtained at room temperature. We found that the emission intensity decreased with increasing temperature for all compounds. This same behavior was found by Liao et. al.<sup>50</sup> and Yelamaggad et al.<sup>49</sup> in the study of the temperature-dependent emission spectra of DLCs derived from platinum(II) complexes of pyridyl pyrazolate chelates and tris(N-salicylideneaniline)s respectively. In fact there are only few works treating the temperature-dependent emission of DLCs in literature.<sup>49-52</sup> A graph of the emission intensity of the maximum wavelength versus the temperature is shown in Figure 3b. It is known that semiconductors

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behave in such a manner, with a decrease in fluorescence intensity due to a larger quantity of self-quenching aggregates and also non-radiative decay processes that take place with increasing temperature.<sup>53</sup> In our previous studies on the theoretical and X-ray structure of the tristriazolotriazine core<sup>41</sup> we found that the three peripheral phenyl rings are twisted with respect to the triazine core, and thus the  $\pi$ -stacking is sterically inhibited in the solid phase. The corecore mean distance observed in the XRD analysis in the Col<sub>h</sub> phase (around 3.5 Å) is suitable for  $\pi$ -stacking. Thus, we believe that the transition from the solid to LC phase is accompanied by a reorganization of the molecule to acquire a more planar conformation, in which the intermolecular  $\pi$ -stacking is likely to quench the emission. The quenching of fluorescence by intermolecular  $\pi$ -stacking may be occurring together with non-radiative decay processes, due to an increase at a higher temperature in segment and molecular mobility and consequently the increased possibility of the excited state to relax via internal conversion or transfer of the energy by collision.

For **1** and **2**, a significant decrease in the emission intensity is evident when the samples pass from the solid to  $Col_h$  phase. Also, there were small changes in the spectra profiles before and after the Cr-Col<sub>h</sub> transition. For compound **2** red-shifted shoulders at 403 and 415 nm became evident above 45 °C, whose can be related to the chirality present in this compound and and specific molecular interactions that leads aggregation of molecules when the compound enters the mesophase. Compound **3** is in a Col<sub>h</sub> phase at room temperature and, interestingly, heating up to 60 °C did not lead to any significant loss in the emission intensity, which started to decrease linearly with heating above this temperature. The branched alkyl chains in **3**, prevented the loss of the emission intensity even up to relatively high temperatures. This may be due to a more hindered packing of these molecules, avoiding the presence of a larger quantity of self-quenching

aggregates at a certain temperature. Compound **3** presented a less structured spectra with a 10 nm blue-shift in the emission maximum wavelength related to that recorded at room temperature.



Figure 3 a) Emission spectra of compounds 1-3 recorded during heating from solid to  $Col_h$  and

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to isotropic phase. b) Plot of the emission intensity of the maximum wavelength versus the temperature for samples of **1-3**. Results for compound **5** can be found in the SI.

At higher temperatures, with the isotropization of the columns, the drop in the emission intensities became less intense and showed a tendency to stabilize at a minimum value. With the exception of compound **5**, which demonstrated thermal decomposition in this study, all compounds showed the same profile in the cooling process from the isotropic to the solid phase (the emission increasing with decreasing temperature).

On the basis of the helical model proposed for the columnar liquid crystals,<sup>44</sup> we measured the circular dichroism (CD) in the mesophase for compounds **1** and **2** (Figure 4).The aim was to determine whether the chirality of the chiral alkyl chains is transmitted to the supramolecular organization of the mesophase and whether this may be related to a helical disposition of the molecules along the column.

The CD measurements were performed on films prepared on untreated quartz slides, heated until the isotropic phase and slowly cooled. The spectra are the result of the averaging of six CD spectra recorded at different film orientations obtained by rotating (in-plane) the sample cells by 60° relative to the light beam. The spectra found were almost identical for all orientations of the sample, which excludes the possibility of linear dichroism effects due to macroscopic orientation.<sup>55</sup> As expected, compound **1** was not active in terms of CD because of the absence of chirality in the structure. Compounds **3**, **4** and **5** also showed no signals on the CD spectra.

The CD spectra for compound **2** displayed an intense signal (for tristriazolotriazine  $\lambda_{max}$ = 327nm), which is in agreement with the helical disposition of the chromophores<sup>56</sup> in the liquid crystalline phase. Moreover, compound **2** presented significant CD even before the thermal treatment, due to the wide range of low temperatures associated with the mesophase. The

relationship between the appearance of CD bands and the formation of chiral superstructures whose sign is related by the configuration of the stereogenic centers in the alkoxy chain is clearly confirmed by the CD spectra profile.

The optical value for the energy gaps ( $E_g$ ), between HOMO and LUMO, were calculated from film absorption spectra and found to be as high as 3.5 eV for the studied compounds (Table 2). Cyclic voltammetry of the DLC compounds showed only a non-reversible oxidation wave, peaking at between 1.6 and 1.9 V (*vs.* Ag/AgCl). The results of the electrochemical study suggested that the tristriazolotriazine core potentially has electron-transporting characteristics.

**Conductivity Measurements in the Col**<sub>h</sub> **Phase.** The electrical characterization of columnar liquid crystals is essential to evaluate their applications as charge or ion conductors. The a.c. impedance spectroscopy is a useful technique that provides such information by applying an alternate voltage with a frequency that ranges from MHz to mHz. The results are usually interpreted in terms of equivalent circuits consisting of electrical components as resistors, capacitors and inductors<sup>57</sup>. Therefore, impedance measurements were performed in order to obtain information on the conductivity of these compounds in the LC state. Figure 5 shows the complex impedance graphs (Z'' vs. Z') and the POM textures of compounds 1 and 3 in the Col<sub>h</sub> phase. The plots show the well-defined semi-circle which is characteristic of a circuit consisting of a resistor and a capacitor in parallel, where *R* is interpreted as the bulk resistance, and the inclined lines at lower frequencies indicate the existence of interfacial effects at the electrodes. All the investigated compounds showed the same behavior. From the *R* values the conductivity could be calculated using  $\sigma = d/(R.A)$ , where *d* is given by the thickness of the spacers, which provides the distance between the electrodes, and *A* is their surface area (in all cells this was

around 2.4 cm<sup>2</sup>). The values obtained for the calculated conductivity  $\sigma$  in the Col<sub>h</sub> phase are 5.8x10<sup>-8</sup>, 1.4x10<sup>-8</sup>, 2.1x10<sup>-8</sup> and 1.0x10<sup>-9</sup> S.m<sup>-1</sup> for compounds **1**, **2**, **3** and **5**, respectively.

A careful analysis of the capacitance curves as a function of the frequency, where we observed a huge increasing of the real capacitance (about three orders of magnitude, see SI) at the low frequency regime, suggested that the obtained conductivity is mostly ionic dominated. In this case, the straight line after the semicircle is related to the double layer capacity due to the ions at the interface of the electrodes.<sup>58</sup> The low values obtained here are probably related to relatively high radii of the ionic species. Chemical ionic impurities, resulting from the synthesis procedures, are usually present in liquid crystalline semiconductors, where the ionic transport can be dominant for a concentration of ions over a few ppm.<sup>59</sup> Our values are about four orders of magnitude lower than values in the literature for columnar ionic liquids<sup>29</sup>, where the incorporation of lithium salts in those columnar materials enhanced their ionic conductivity measured along the columnar direction. The POM textures (Figure 5) show that the investigated cells of 1 and 3 after annealing presented planar domains, indicating that the homeotropic alignment was not so efficient. This means that our compounds may find applications as ionic conductors since the conducting properties can be optimized by the addition of proper salts and alignment of the columns.



Figure 4 (a) CD spectra recorded on thin films of compounds 1 (dashed line) at 110°C and 2 (solid line) at 60°C, and respective (b) absorbance spectra.

**Morphology aspects of thin films**. We used Atomic Force Microscopy (AFM) to investigate the morphology aspects of spin-coated films of the LC compounds (1, 2, 3 and 5). From the measurements we obtained the mean surface roughness and the film thickness. Electronic applications require homogeneous films with low surface roughness. Figure 6 shows representative images of compound 5, where a homogeneous covering of the surface was observed, even for images as large as 50  $\mu$ m x 50  $\mu$ m. The same behavior was observed for the other compounds investigated. The values obtained for the mean surface roughness (RMS) and the thickness are presented in Table 3 for all compounds, where it is clear that, under the same experimental conditions, 1 displays the highest roughness and 3 the highest thickness. The higher roughness of 1 may be related to a more crystalline profile, due to its straight and less bulky peripheral alkyl chain. Compounds 2 and 3, with branched alkyl groups, and 5 with bulky

alkoxybenzyl peripheral groups are more amorphous materials and present smoother surfaces, particularly **3** and **5**. Compound **3**, a room temperature LC, displays the greatest thickness. It is worth to noting that the roughness values indicate that these surfaces are quite smooth and appropriate for electronic purposes. In addition, the thickness can be reduced by increasing the spinning velocity or by decreasing the concentration of the deposited species.



**Figure. 5** Left side: (a) Impedance Z'' vs. Z' plots of compounds 1 and 3 captured in their Col<sub>h</sub> phases. R indicates the resistance values used for the conductivity calculations. Right side: POM images with 100x amplification of the cells used for impedance measurements, containing compounds 1 (b) and 3 (c) in the Col<sub>h</sub> phase after annealing. The images indicate the presence of planar domains.



**Figure 6** AFM images of compound **5**. Image size of (a) 50 μm x 50 μm and (b) 15 μm x 15 μm in a 3D perspective.

Г <b>able 3.</b> Mean surface roughness (RMS	) and thickness of the spin-coated films.
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Compounds	1	2	3	5
RMS (nm)	4.3	1.5	0.6	0.7
Thickness (nm)	168±10	150±10	240±10	165±10

## CONCLUSIONS

We have synthesized and characterized a series of luminescent columnar liquid crystalline compounds based on a tris[1,2,4]triazolo[1,3,5]triazine core. On the basis of the results obtained, these materials offer an easily synthesized alternative to other *N*-heterocycle cores based columnar LC compounds with the advantage of possessing a low temperature stable Col<sub>h</sub> phase and the capacity to form a helical architecture, when containing chiral peripheral chains. They also present an intense blue luminescence, being characterized as high energy gap (~3.5 eV) blue emitter materials. The electron-accepting capability of the tristriazolotriazine core, confirmed by voltammetry analysis, along with the formation of an efficient  $\pi$ -bonding interaction of the

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heteroaromatic and aromatic portions in the columnar phase, detected by optical and XRD analysis, makes these materials good candidates for application in optoelectronic devices, such as organic light-emitting diodes, field effect transistors, and photovoltaic cells.

## ACKNOWLEDGMENT

We thank the following institutions for financial support: CAPES/PNPD, CNPq/PRONEX/FAPESC, INCT/INEO and INCT-Catálise. The XRD experiments were carried out in the Laboratório de Difração de Raios-X (LDRX-CFM/UFSC). We also thank Dr. Fernando Ely (CTI, Campinas-SP, Brazil) for the cells used in the conductivity experiments, Dr. José Luis Serrano and Dr. Teresa Sierra (Universidad de Zaragoza-CSIC) for the free access to the CD instrument, and Dr. Hernán Terenzi for free access to MALDI-TOF and micrOTOF-Q II APCI-Qq-TOF instruments at CEBIME-UFSC.

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