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# Soft Matter

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Tetra- and hexacatenar amide compounds containing a linear centrosymmetric benzobisthiazole core were synthesized with good yields. These compounds were characterized and their structures confirmed by elemental analysis, FT-IR, Maldi mass and NMR spectroscopies. All compounds exhibited excellent thermal stability up to 330°C. The tetracatenar series containing a double substitution in the meta positions did not show mesomorphic behaviour, whereas the hexatenar and tetracatenar series having a double substitution in the meta and para positions showed liquid crystals properties with optical textures typical of columnar mesophases corroborated by POM analysis. The mesomorphic properties were dependent on the length, number and position of alkoxy chains attached at the end of the rigid core. XRD studies of the hexactenar series showed the hexagonal columnar structure of the mesophases. Photoluminescence properties in solution were observed in the visible region, with good quantum yields. In solid state, these compounds behave as blue emitters and they are able to change colour with acid or base addition. The hexacatenar benzobisthiazole compound with an alkoxy chain of 14 carbons presented properties of a super gelator in chloroform, leading to the formation of a fluorescent organogel material with fluorescent emission in the blue region.

## Introduction

The scientific interest in benzobisthiazole (BBZT) compounds is largely linked to their potential applications in the fabrication of nonlinear optical devices, light-emitting diodes, transistors equipment, photo-voltaic and solar cells<sup>1-7</sup>. The electronic delocalization enhanced by the presence of the heterocycle and benzene ring in BBZT compounds can explain properties like high fluorescence, electron transport and nonlinear optics<sup>3,7-11</sup>. One of the major inconvenient in using BBZT compounds is the synthesis protocol which required harsh conditions. However, recently, BBZT compounds were obtained with good yields under mild conditions<sup>4,12-15</sup>, and investigations based on their electronic applications could be expected. The challenge for such investigations is the design and the synthesis of BBZT compounds able to form materials keeping or improving the electronic properties of BBZT systems<sup>1</sup>.

Liquid crystal materials are known for their applications in

devices as organic light-emitting diodes (OLEDs), lasers or photovoltaic cells<sup>16-20</sup>. Among the different mesomorphic structures, the most suitable mesogens with properties in electron transport are those presenting a columnar phase<sup>21-30</sup>. Electron transport in this kind of structure occurs due to the presence of a rigid core, formed by an overlapping aromatic  $\pi$  system, leading to the formation of molecular pathways in one dimension. Polycatenar  $\mathsf{compounds}^{21,22,26}$  belong to a class of liquid crystals, able to generate different mesophases (nematic, smectic, cubic and columnar systems). Their structure corresponds to a long rod-like core ending in two half-disc-shaped moieties with two or more aliphatic chains. In order to achieve columnar liquid crystals (CLC), the structure of the polycatenar compounds should incorporate two or three paraffinic side chains at each end, leading to a tetraand hexacatenar system respectively<sup>22</sup>. Recently<sup>12</sup>, we reported the synthesis and the mesomorphic study of polycatenar columnar liquid crystals which incorporate in the core, through ester bond, a benzobisthiazole unit. These products showed to be highly thermally stable within the temperature range in which they exhibit mesomorphism and, due to the presence of a benzobisthiazole unit. they present photoluminiscent properties in the visible region with good quantum yields.

Gel materials are usually used in the pharmaceutical, cosmetic and food sector due to their soft properties<sup>31-35</sup>. Although it is not always possible to predict the ability of a compound to form a gel, structural studies allow to establish some important required factors<sup>33,34,36,37</sup>. One of these factors is the intermolecular

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interactions<sup>36,38</sup>, being the more important one the hydrogen bond, usually generated from carboxylic acid, hydroxyl or amide functional groups. Another factor is linked to the presence of some specific chemical group  $^{32,36,39}$ : (i) an aromatic central unit allowing the stacking effects, (ii) alkoxy long chains for their role in the solubility or precipitation in a particular solvent, and (iii) polar groups allowing to generate dipole-dipole interactions. Nowadays, the gel science<sup>33,37,39</sup>, especially in organic chemistry, offers promising investigations in the field of electronics. Interesting efforts have been focused on the preparation and study of organic gelators exhibiting  $\pi$  systems, which are able to form supramolecular organizations with nano to microscale size and could lead to potential applications in electronic devices<sup>15,31,33,37,40</sup>. The BBZT compounds are considered as  $\pi$  systems, able to generate dipole-dipole interactions, and therefore their incorporation in adequate organic molecules could lead to very promising compounds able to self-assembly in organic solvents as gel materials.

The aim of this article is orientated to the study of polycatenar compounds containing a linear centrosymmetric benzobisthiazole group, able to form liquid crystal and gel materials. Based on our previous results, a new synthetic approach to obtain such hybrid materials was designed. The methodology involves the incorporation of amide groups, known for favouring hydrogen bond. The properties of the polycatenar compounds are usually dependent of the numbers, positions and lengths of the side chains<sup>21</sup>. These factors are considered very determinant as spacefilling requirements in order to obtain a molecular packing efficiency, especially for the formation of liquid crystal materials. Consequently, in this article, three series of compounds were considered and synthesised: series 2a-c (tetracatenar meta, para), series 3a-c (tetracatenar meta, meta) and series 4a-c (hexacatenar meta, para, meta) (scheme 2). The molecular structure of these compounds was characterized by spectroscopic analyses and their thermal behaviour was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The optical properties in solution and solid state were also analysed. Finally, the liquid crystal/gel formation and their respective characterizations are discussed, showing the important effect of the side chains on the polycatenar compounds.

## Experimental

#### Materials

All reagents were purchased from Aldrich Chemical Co or Merck, and were used without further purification. All solvents were dried under standard conditions.

## **Characterization techniques**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer, with CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvents and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded with a Nicolet Magna 550 spectrometer. MALDI experiments were carried out on a Bruker Microflex. Thermogravimetric (TG) measurements were conducted with a STA 625 system in platinum pans at prescribed heating rates of 10 °C

min<sup>-1</sup> in the range 25–650 °C under a steady flow of nitrogen (42 mL min<sup>-1</sup>). Transition temperatures and textures of mesophases were determined by a polarised optical microscopy (POM) using an Olympus BX51 optical microscope equipped with an Olympus U-TV0.5XC-3 polariser and a Linkan T95-PE heat stage. Transition temperatures and enthalpies were investigated by DSC using a TA Instrument Q1000 calorimeter. Samples were encapsulated in aluminium pans and observed at scanning rate of 10°C min<sup>-1</sup> on heating and cooling. The instrument was calibrated using an indium standard (156.6 °C, 28.44 Jg<sup>-1</sup>) under nitrogen atmosphere. XRD patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu K $_{\alpha}$  beam. The samples were held in Lindemann glass capillaries (0.9 mm diameter) and heated with a high-temperature attachment. The patterns were collected on flat photographic film perpendicular to the X-ray beam and spacing was obtained via Bragg's law. Ultraviolet-visible absorbance measurements were made with UV4-200 of ATI-Unicam spectrometer of dual beam between 200 and 600 nm. Luminescence measurements were obtained using a Perkin-Elmer LS50B between 340 and 700 nm. Scanning electron microscopy (TEM) was carried out using a JEOL 1200EXII instrument with an activation voltage of 120 kV. Solid-state emission spectra were acquired at room temperature by a Zeiss LSM 780 NLO spectral microscope at the CMA-Bio Bio (Centro de Microscopía Avanzada Bio Bio) belonging to the University of Concepción. A 405 nm wavelength excitation laser and a 20× air objective were used in all cases. The spectral image was created from 44 images obtained in the emission range (412-657 nm) every 5.6 nm. The methodology used to acquire emission spectra under a microscope was already published<sup>29</sup>. Briefly, after excitation, the emission light is decomposed and its spectral components are detected by a spectral detector. Forty four emission images are taken at pre-selected wavelength and their superposition form a spectral image. From the spectral image, the emission spectra can be reconstructed from each pixel. The emission spectra composed by 44 points (obtained from 4 positions in the image) were normalized and averaged. A solution of fluorescein at pH 9 was used as standard for instrument calibration and comparison of the data from cuvette and microscope. The emission spectra of the standard solution acquired in the cuvette and in the microscope show the maximum at 510 nm. For sample preparation, thin film were deposited and dried on an optical glass and covered with a second cover glass.

#### Synthesis and Characterization of the di-amine compound 1

4-nitrobenzoic acid (1.62 g, 9.67 mmol) was dissolved in 60 mL of dry dichloromethane and then oxalyl dichloride (3.07 g,24.2 mmol) and a drop of dimethyl formamide (DMF) as catalyst were added. The mixture was stirred at room temperature for 12 h under nitrogen atmosphere. The solution was concentrated to remove the excess of oxalyl dichloride, and the residue was dissolved in 40 mL of dry N-methyl-2-pyrrolidone (NMP). Then, a solution of 2,5-diamino-1,4-benzenedithiol dihydrochloride (1.13 g, 4.60 mmol) and 150 mL of NMP was slowly added. The resulting mixture was stirred for 48 h at 140 °C. The mixture was then cooled to room temperature, poured into ice-water, and neutralized with 10% NaOH<sub>(aq)</sub>. The collected brown solid was washed with water, and then washed twice with boiling ethanol to give the intermediate

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product I in 85% yield as a yellow solid and characterized by FT-IR spectroscopy.

FT-IR (KBr) cm<sup>-1</sup>: 1518 y 1343 cm<sup>-1</sup> (NO<sub>2</sub>). Elemental analysis data (%)for  $C_{20}H_{10}N_4O_4S_2$ , calculated: C 55.29, H 2.32, N 12.90, S 14.76; found: C 55.22, H 2.37, N 12.94, S 14.70.

The intermediate compound I (1.66 g, 3.82 mmol) was dispersed in 100 mL of glacial acetic acid at 100 °C. Subsequently to this dispersion, SnCl<sub>2</sub>xH<sub>2</sub>O (7.93 g, 38.2 mmol) dissolved in 16 mL of concentrated hydrochloric acid was added. The mixture was refluxed for 15 h, then it was diluted in water (600 mL) at 60 °C and neutralized with 10% NaOH<sub>(aq)</sub> at that temperature. The collected yellow solid was washed with water and then washed with methanol (50 mL) to give 1.43 g of **1** corresponding to 92% yield.

FT-IR (KBr) cm<sup>-1</sup>: 3228 y 3341 (NH<sub>2</sub>). Elemental analysis data (%)for  $C_{20}H_{14}N_4S_2$ , calculated: C 64.15, H 3.77, N 14.96, S 17.12; found: C 64.13, H 3.79, N 14.99, S 17.09. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm): 5.94 (s, 4H, NH<sub>2</sub>, proton (a)), 6.68 (AA'BB', 4H, *J* = 8.0 Hz, aromatic proton (b)), 7.77 (AA'BB', 4H, J = 8.0 Hz, aromatic proton (c)), 8.51 (s, 2H, aromatic proton (d)). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm): 113.7 (b), 114.2 (h), 120.1 (d), 128.9 (c), 133.1 (f), 151.4 (g), 152.4 (a), 168.4 (e)

# Synthesis and Characterization of the amide compounds corresponding to series 2, 3 and 4

All amides of series **2a-c**, **3a-c** and **4a-c** were prepared similarly according to the procedure described in a general method.

General method: 3,4-di-n-, 3,5-di-n-, and/or 3,4,5-tri-nalkoxybenzoic acid (1.68 mmol) was dissolved in 40 mL of dry dichloromethane and then oxalyl dichloride (0.32 g, 2.52 mmol) with a drop of DMF as catalyst were added. The mixture was stirred at room temperature for 12 h under nitrogen atmosphere. The solution was concentrated to remove the excess of oxalyl dichloride and the residue was dissolved in 30 mL of dry tetrahydrofuran (THF). A solution of compound **1** (0.311 g,  $8.27 \times 10^{-1}$  mmol), 1.0 mL of triethylamine (TEA) and 4-(N,N-dimethyl) aminopyridine (DMAP) as catalyst, dissolved in NMP (40 mL) was added on the acid chloride solution. The mixture was stirred at room temperature for 48 h under nitrogen atmosphere and then was poured into a mixture of ice-water. The solid was filtered off, washed several times with water and purified by column chromatography by eluting with chloroform to yield pure 2a-c to 4a-c compounds as paled yellow solids.

*Characterization of compound* **2a**. 63% yield. FT-IR (KBr) cm<sup>-1</sup>: 3319 (N–H), 1652 (C=O). Elemental analysis data (%) for  $C_{74}H_{102}N_4O_6S_2$ , calculated: C 73.59, H 8.51, N 4.64, S 5.31; found: C 73.42, H 8.59, N 4.82, S 5.25.

*Characterization of compound* **2b**. 65% yield. FT-IR (KBr) cm<sup>-1</sup>: 3318 (N–H), 1653 (C=O). Elemental analysis data (%) for  $C_{82}H_{118}N_4O_6S_2$ , calculated: C 74.61, H 9.01, N 4.24, S 4.86; found: C 74.46, H 9.12, N 4.11, S 4.70.

Characterization of compound **2c**. 66% yield. FT-IR (KBr) cm<sup>-1</sup>: 3321 (N–H), 1651 (C=O). Elemental analysis data (%) for  $C_{90}H_{134}N_4O_6S_2$ ,

calculated: C 75.48, H 9.43, N 3.91, S 4.48; found: C 75.35, H 9.31, N 3.55, S 4.37.

*Characterization of compound* **3***a*. 69% yield. FT-IR (KBr) cm<sup>-1</sup>: 3317 (N–H), 1652 (C=O). Elemental analysis data (%)for  $C_{74}H_{102}N_4O_6S_2$ , calculated: C 73.59, H 8.51, N 4.64, S 5.31; found: C 73.52, H 8.55, N 4.60, S 5.27. MALDI-TOF-MS calculated for  $C_{74}H_{102}N_4O_6S_2$  [M+H]<sup>+</sup> 1207.7, found 1207.8.

Characterization of compound **3b**. 71% yield. FT-IR (KBr) cm<sup>-1</sup>:3316 (N–H), 1653 (C=O).Elemental analysis data (%) for  $C_{82}H_{118}N_4O_6S_2$ , calculated: C 74.61, H 9.01, N 4.24, S 4.86; found: C 74.60, H 8.97, N 4.26, S 4.80. MALDI-TOF-MS calculated for  $C_{82}H_{118}N_4O_6S_2$  [M+H]<sup>+</sup> 1319.9, found 1319.9.

*Characterization of compound* **3***c*. 70% yield. FT-IR (KBr) cm<sup>-1</sup>:3320 (N–H), 1654 (C=O). Elemental analysis data **(%)** for  $C_{90}H_{134}N_4O_6S_2$ , calculated: C 75.48, H 9.43, N 3.91, S 4.48; found: C 75.39, H 9.45, N 3.97, S 4.46. MALDI-TOF-MS calculated for  $C_{90}H_{134}N_4O_6S_2$  [M+Na]<sup>+</sup> 1454.0, found 1454.1.

*Characterization of compound* **4a**. 74% yield. FT-IR (KBr) cm<sup>-1</sup>:3305 (N–H), 1655 (C=O). Elemental analysis data (%) for  $C_{94}H_{142}N_4O_8S_2$ , calculated: C 74.26, H 9.41, N 3.69, S 4.22; found: C 74.20, H 9.44, N 3.73, S 4.17. MALDI-TOF-MS calculated for  $C_{94}H_{142}N_4O_8S_2$  [M+Na]<sup>+</sup> 1543.0, found 1543.0. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.88 (m, 18H, –CH<sub>3</sub> proton (a)), 1.19–1.79 (m, 48H, –CH<sub>2</sub>– proton (b)), 3.98 (m, 12H, OCH<sub>2</sub> proton (c)), 7.06 (s, 4H, aromatic proton (d)), 7.75 (AA'BB', 4H, aromatic proton (g)) 8.15 (s, 2H, N–H proton (e)), 8.38 (s, 2H, aromatic proton (h)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.3 (a); 22.8, 26.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.5, 32.0, 32.1(b); 69.6 (c); 73.7 (d); 106.0 (g), 115.2 (q); 120.5 (k); 123.6 (I); 129.5 (h); 129.6 (m); 134.4 (o); 140.8 (e); 141.9 8 (j), 152.2 (p); 153.4 (f); 166.0 (i); 168.2 (n).

*Characterization of compound* **4b**. 75% yield. FT-IR (KBr) cm<sup>-1</sup>:3306 (N–H), 1657 (C=O). Elemental analysis data **(%)** for  $C_{106}H_{166}N_4O_8S_2$ , calculated: C 75.40, H 9.91, N 3.32, S 3.80; found: C 75.36, H 9.95, N 3.37, S 3.77. MALDI-TOF-MS calculated for  $C_{106}H_{166}N_4O_8S_2$  [M+Na]<sup>+</sup> 1711.2, found 1711.1. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.88 (m, 18H, –CH<sub>3</sub> proton (a)), 1.16–1.79 (m, 60H, –CH<sub>2</sub>– proton (b)), 4.02 (m, 12H, OCH<sub>2</sub> proton (c)), 7.07 (s, 4H, aromatic proton (d)), 7.79 (AA'BB', 4H, aromatic proton (c)), 8.45 (s, 2H, N–H proton (e)), 8.08 (AA'BB', 4H, aromatic proton (g)), 8.45 (s, 2H, aromatic proton (h)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.2 (a); 22.9, 26.2, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.5, 32.1 (b); 69.7 (c); 73.8 (d); 106.0 (g); 115.3 (q); 120.3 (k); 123.7 (I); 128.7 (h); 129.6 (m); 134.5 (o); 140.9 (e); 141.8 (j); 152.3 (p); 153.5 (f); 165.9 (i); 168.3 (n).

*Characterization of compound* **4c**. 75% yield. FT-IR (KBr) cm<sup>-1</sup>:3308 (N–H), 1657 (C=O). Elemental analysis data **(%)** for C<sub>118</sub>H<sub>190</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>, calculated: C 76.32, H 10.31, N 3.02, S 3.45; found: C 76.30, H 10.35, N 3.11, S 3.40. MALDI-TOF-MS calculated for C<sub>118</sub>H<sub>190</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 1879.4, found 1879.6. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.89 (m, 18H, –CH<sub>3</sub> proton (a)), 1.16–1.79 (m, 72H, –CH<sub>2</sub>– proton (b)), 4.03 (m, 12H, OCH<sub>2</sub> proton (c)), 7.07 (s, 4H, aromatic proton (d)), 7.79 (AA'BB', 4H, aromatic proton (f)), 7.97 (s, 2H, N–H proton (e)), 8.09 (AA'BB', 4H, aromatic proton (g)), 8.47 (s, 2H, aromatic proton (h)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 14.2 (a); 22.8, 26.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.6, 32.2 (b): 69.8 (c): 73.9 (d): 106.2 (g): 115.2 (c):

29.7, 29.8, 30.6, 32.2 (b); 69.8 (c); 73.9 (d); 106.2 (g); 115.2 (q); 120.3 (k); 123.8 (l); 128.8 (h); 129.7 (m); 134.7 (o); 140.8 (e); 141.9 (j); 152.4 (p); 153.7 (f); 165.9 (i); 168.5 (n).

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#### **Gel Formation**

The gel preparations of the products **2a-c**, **3a-c** and **4a-c** were carried out using solvents as chloroform and tetrahydrofuran which allowed dissolving the products. Concentrations of 5, 2.5, 1.5, 1 and 0.5% were prepared in glass vials. Once the product precipitated, the glass vial is inverted, in order to confirm the gel formation.

## **Results and discussion**

#### Synthesis description and spectroscopic characterizations

The synthesis of amide compounds incorporating a linear centrosymmetric benzobisthiazole unit has been carried out starting from the di-amine precursor **1**, obtained by a condensation reaction between one equivalent of 2,5-diamino-1,4-benzenedithiol dihydrochloride<sup>12</sup> and two equivalents of 4-nitrobenzoyl chloride, followed by a reduction reaction of the nitro functions of the intermediate **I**, as indicated in scheme **1**.

The precursor **1** was obtained with good yields and its structure was confirmed by elemental analysis and spectroscopic methods. As expected and seen in Figure **1**, the <sup>1</sup>H NMR spectrum of precursor **1** dissolved in DMSO-d<sub>6</sub> showed four signals, corresponding to the amine and aromatic protons. A clear system AA'BB' can be observed, attributed to the side aromatic rings, and a singlet signal

corresponding to the protons of the central ring can be distinguished. The <sup>13</sup>C NMR spectrum confirmed the structure of precursor **1** exhibiting the expected signals corresponding to the eight magnetically non-equivalent carbon atoms (figure 1). Moreover, two strong bands at 3228 and 3341 cm<sup>-1</sup> attributed to the NH<sub>2</sub> groups were identified by FT-IR spectroscopy.



## **Figure 1.** NMR spectra of precursor **1**: a) $^{1}$ HNMR and b) $^{13}$ C NMR



The amide compounds of series **2a-c**, **3a-c** and **4a-c** including the benzobisthiazole unit were synthesised by a condensation reaction (see scheme 2) between one equivalent of the precursor **1** and two equivalents of the corresponding 3,4-di-, 3,5-di- or 3,4,5-tri-n-

alkoxybenzoyl chloride in NMP and dichloromethane as solvents, employing triethylamine (TEA) and 4-(N,N-dimethyl)aminopyridine (DMAP) as base and catalyst respectively.

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3 (a-c): X=OC<sub>n</sub>H<sub>2n+1</sub>, Y=H 4 (a-c): X=Y=OC<sub>n</sub>H<sub>2n+1</sub> n=10, 12, 14 Scheme 2

The structure of the amides 2a-c to 4a-c was clearly evidenced by the absorption bands of the amide groups observed in FT-IR spectra, and elemental analysis. Since 2a-c showed to be insoluble in common organic solvents, their structural characterization was restricted to the techniques mentioned previously. In the case of the **3a-c** series, showing partial solubility in common organic solvents, additional characterisation corresponding to the determination of the molecular weight was achieved by Maldi mass spectrometry. On the other side, series of amides 4a-c were highly soluble in solvents such as dichloromethane, chloroform and

tetrahydrofuran and, hence, they were characterized by <sup>1</sup>H and <sup>13</sup>C NMR. Figure 2 shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4a** as a representative example of the corresponding series. Both NMR spectra confirmed the expected structure, showing the central benzobisthiazole ring linked to the amide functions. The system AA'BB' corresponding to the benzobisthiazole unit was observed by <sup>1</sup>H NMR. The proton integrations indicate an excellent correlation among the proton proportions of each signal. In the same way, <sup>13</sup>C NMR showed the presence of all the expected carbon signals.



Figure 2. NMR spectra of 4a: a) <sup>1</sup>HNMR and b) <sup>13</sup>C NMR.

#### Thermogravimetric studies

The amide series **2a-c** to **4a-c** were submitted to thermogravimetric analysis under nitrogen. No apparent weight loss between 100 °C and  $\sim$  330-370 °C was observed, indicating that no solvent was

occluded. The three series exhibited high thermal stability up to 330 ° C. As indicated in figure 3, their thermal decomposition occurred in one step process. It starts in a temperature range of 330-370 °C with a 1% weight loss and ends in a temperature range of 490-500 °C with a weight loss between 65-90%.

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Figure 3. Thermal decomposition profiles of 2a-c, 3a-c y 4a-c.

The temperature range of thermal decomposition for the amide series **2** explains why the mesomorphic range and the corresponding enthalpies of this series could not be determined by DSC analysis (table 1). The ester analogues, previously reported<sup>12</sup>, present also similar temperature ranges of thermal decomposition, showing that the amide groups do not really affect the thermal stability in such compounds.

## **Mesomorphic properties**

The mesomorphic behavior of compounds 2a-c to 4a-c was studied by polarized light optical microscopy (POM) and thermal analysis (differential scanning calorimetry DSC). The temperatures and enthalpies of phase transitions are summarized in Table 1, and figure 4 presents the textures observed through POM. The **2a-c** and 4a-c series exhibit mesomorphic properties, while the 3a-c series shows only crystalline phases. Textures observed by POM for compounds 2a-c, in the heating process, are consistent with the presence of columnar mesomorphism (figure 4). In the case of the 4a-c series, their textures could be seen only after a friction process applied on the samples because they present a homeotropic orientation: as the columns are aligned in the direction of propagation of the polarized light, no birefringence could be observed in these mesophases, unless they were disturbed by a friction process. As observed in the ester series<sup>12</sup>, the mesomorphic behaviour seems to be dependent on the number, position and length of the flexible side chains attached at the end of the central rigid unit. The melting temperatures of the compounds in series 2a-

c decrease slightly as the chain length increases (303 ° C for 2a, 294 ° C for 2a and 279 ° C for 2c). The same trend was observed for the series 3a-c (228 °C for 3a, 218 °C for 3b and 179 °C for 3c) and 4a-c (193 °C for 4a, 175 °C for 4b and 169 °C for 4c). The melting temperatures of the similar ester compounds reported previously<sup>12</sup> are much lower, due the higher polarity and intermolecular interactions (hydrogen bonding) present in the amide functions. The clearing temperatures and mesomorphic ranges for the series 2a-c could not be determined, since they decompose before reaching such temperature, in accordance with the results obtained from TGA analysis. In the case of the hexacatenar 4a-c series, it is possible to observe that the clearing temperatures decrease upon lengthening the alkoxy chains with values of 213 °C for 4a, 211 °C for 4b and 208 °C for 4c, whereas mesomorphic ranges increase from 4a to 4c, with ranges of 20 °C for 4a, 36 °C for 4b and 39 °C for **4c**. Compared to the hexacatenar ester series reported previously<sup>12</sup>, the hexacatenar amide series showed higher clearing temperatures and a broader mesomorphic range, due to the same reasons mentioned previously about the characteristics of the amide function. It is important to underline that, as stated in the case of the tetracatenar meta, meta ester compounds, the tetracatenar meta, meta amide compounds (3a-c) did not show mesomorphic behaviour. With this result, we can suggest that a double substitution in the meta positions at the end benzene rings disfavours the formation of mesophases, due to a lower packing efficiency and unsatisfied space-filling requirements of the alkoxy groups.

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**Figure 4.** Optical textures (magnification 200 X) observed under POM in the heating cycle for the series **2** and in the cooling cycle after friction for the series **4**: a)  $Col_x$  phase at 310 °C of **2a**, b)  $Col_x$  phase at 305 °C of **2b**, c)  $Col_x$  phase at 295 °C of **2c**, d)  $Col_h$  phase at 172 °C of **4a**, e)  $Col_h$  phase at 175 °C of **4b**, f)  $Col_h$  phase at 183 °C of **4c**.

**Table 1.** Phase-transition temperatures (°C), enthalpies (KJ mol<sup>-1</sup>, in parentheses) as determined by DSC, scanning rate 10 °C min<sup>-1</sup> and  $T_{id}$  (°C, temperature of initial decomposition) for compounds **2a–c** to **4a–c**.

Phase Transitions	$T_{id}$
Cr 303 (-) Col <sub>x</sub> * (-) Dec.	363
Cr 294 (106.7) Col <sub>x</sub> * (-) Dec.	358
Cr 279 (89.8) Col <sub>x</sub> *(-) Dec.	356
Cr 228 (76.6) I	240
l 212 (77.7) Cr	349
Cr 218 (62.3) I	260
l 198 (61.4) Cr	500
Cr 179 (40.4) I	257
l 163 (39.8) Cr	227
Cr 193 (24.7) Col <sub>h</sub> 213 (7.3)I	255
l 192 (0.9) Col <sub>h</sub> 141 (18.1) Cr	222
Cr 175 (32.8) Col <sub>h</sub> 211 (8.4) I	367
l 210 (4.9) Col <sub>h</sub> 142 (26.5) Cr	502
Cr 169 (27.3) Col <sub>h</sub> 208 (8.0) I	356
l 203 (4.1) Col <sub>h</sub> 145 (35.3) Cr	330
	Phase Transitions Cr 303 (-) Col <sub>x</sub> * (-) Dec. Cr 294 (106.7) Col <sub>x</sub> * (-) Dec. Cr 279 (89.8) Col <sub>x</sub> * (-) Dec. Cr 228 (76.6) I I 212 (77.7) Cr Cr 218 (62.3) I I 198 (61.4) Cr Cr 179 (40.4) I I 163 (39.8) Cr Cr 193 (24.7) Col <sub>h</sub> 213 (7.3)I I 192 (0.9) Col <sub>h</sub> 141 (18.1) Cr Cr 175 (32.8) Col <sub>h</sub> 211 (8.4) I I 210 (4.9) Col <sub>h</sub> 142 (26.5) Cr Cr 169 (27.3) Col <sub>h</sub> 208 (8.0) I I 203 (4.1) Col <sub>h</sub> 145 (35.3) Cr

## XRD studies

Powder samples of compounds **4a**, **4b** and **4c** were investigated by X-ray diffraction in various sets of conditions. The mesomorphic range of compounds **2a-c** lies well above the upper temperature limit (250 °C) of our X-ray apparatus. The three compounds **4a**, **4b** and **4c** were studied at room temperature after a thermal treatment consisting of heating up to the isotropic liquid and cooling down to room temperature. In addition to this, **4b** and **4c** were initially studied at high temperatures above the transition from the crystalline solid to the fluid mesophase.

In the case of **4a**, the X-ray patterns, indicated in figure 5, were unambiguously characteristic of a hexagonal columnar mesophase. This is revealed by the presence of a set of three sharp maxima in the low-angle region with reciprocal spacing in the ratio 1:  $\sqrt{3}$ : 2, that correspond, respectively, to the (1 0), (1 1) and (2 0) reflections from a 2D hexagonal lattice (Table 2). The measured spacing of the reflections yields a hexagonal lattice constant a = 43.2 Å. The mesomorphic nature of the Col<sub>h</sub> phase is confirmed by the presence in the high-angle region of the broad, diffuse halo characteristic of the molten hydrocarbon chains.

Notes: Cr, crystal phase;  $Col_h$ , hexagonal columnar phase;  $Col_x$ , unidentified columnar phase; I, isotropic phase; \* undetermined transition temperature; Dec. decomposition.

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**Figure 5.** X-ray pattern of **4a** recorded at room temperature after thermal treatment.

For compounds 4b and 4c, the diffractograms are more difficult to interpret. Although the mesophases are retained at room temperature after thermal treatment by fast cooling, some crystallization cannot be avoided and this precludes the reliable indexation of the maxima. Furthermore the thermal behavior of these compounds is very complex and, even at high temperatures in the heating process, it is impossible to get the mesophase free of crystalline phase. Moreover, some diffraction maxima change as a function of the precise experimental conditions. Therefore an unambiguous interpretation of the X-ray cannot be achieved in any of the above-mentioned conditions. However, reliable results were finally obtained at high temperatures by heating up to the isotropic liquid and then irradiating with the X-rays at a temperature above the solid-to-mesophase transition (Table 2). In these conditions, the diffractograms were consistent with a hexagonal columnar mesophase. Indeed for 4b, two low-angle sharp maxima are detected with reciprocal spacing in the ratio 1: v3, that correspond, respectively, to the (1 0) and (1 1) reflections from the hexagonal lattice. Although 4c only yielded one maximum, by analogy to its homologous compounds, it is reasonable that the mesophase is also hexagonal columnar. This is supported by the hexagonal lattice constant a deduced considering this maximum as the (1 0) reflection (Table 2). The a value compares well with the a value for 4b, as the observed difference is consistent with the expected evolution in chain length taking into account the large conformational disorder present at such high temperatures. The large conformational disorder, in turn, accounts for the smaller a values found for these two compounds compared to 4a that was studied at room temperature and therefore must have its chains in a more extended conformation.

Some structural details of the  $Col_h$  mesophase for the three compounds can be deduced from the X-ray results. A discussion of the organization of these non-disc-like compounds in the columnar mesophase is feasible by using some simple calculations. The obtained parameters are not consistent with stacking of single molecules in the columns and therefore, several molecules are needed to generate a disc-like aggregate. The number Z of molecules that generate the proposed supramolecular entity can be estimated by the following equation:

$$Z = \frac{\rho V N_A}{M}$$

where  $\rho$  is the density in g cm<sup>-3</sup>, *V* is the unit cell volume in cm<sup>3</sup>, *N*<sub>A</sub> is Avogadro's number and *M* is the molecular mass in g. Although the exact density of these compounds is not known, its value must be close to 1 g cm<sup>-3</sup> for this kind of organic compound. The unit cell volume is equal to the area *S* of the 2D hexagonal lattice (*S* =  $a^2$  v3/2) multiplied by the mean stacking distance *h*. In the case of **4a**, considering a density of about 1 g/cm<sup>-3</sup>, it is deduced that three molecules occupy a column "slice" of about *h* = 4.7 Å at room temperature. For the other two compounds the same calculations lead to the conclusion that three molecules must occupy a column "slice" of about *h* = 6.1-6.3 Å. The differences in *h* (columns "slice" thickness or mean stacking distance) can be assigned to the space demand at high temperatures due to the larger conformational disorder.

For the three compounds the resulting aggregate must contain the rigid regions of the molecules in the middle and a total number of 18 hydrocarbon chains surrounding the rigid cores. This structural model is similar to that proposed for the analogous esters, the mesophases of which were thoroughly investigated<sup>12</sup>, and thus it is concluded that the type of packing previously proposed for the esters is valid for the analogous amides **4a**, **4b** and **4c**. This result is not unexpected considering the similar molecular structure and identical dimensions of the two series of compounds.

The conclusion of the X-ray diffraction study is that the mesophases of the three compounds investigated is hexagonal columnar. The liquid crystal phase is maintained at room temperature for **4a**, whereas it partially crystallizes at both room temperature (in the cooling process) and high temperatures (in the heating process) for **4b** and **4c**.

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Table 2. Structural parameters of the Col<sub>h</sub> mesophase of compounds 4a, 4b and 4c determined by XRD.

Compound	T (ºC)	$d_{obs}$	$d_{calc}$	h k	Lattice constant (Å)	Mean stacking distance (Å)	Molecules per aggregate
4a	r.t.	37.2 21.7 18.8	37.4 21.6 18.7	10 11 20	a = 43.2	h = 4.7	<i>Z</i> = 3
4b	180	34.6 20.0	34.6 20.0	10 11	<i>a</i> = 40.0	<i>h</i> = 6.1	<i>Z</i> = 3
4c	175	35.5	35.5	10	<i>a</i> = 41.0	<i>h</i> = 6.3	<i>Z</i> = 3

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#### FT-IR Study of the hydrogen bond interactions

In order to examine the presence of intermolecular hydrogen bond interactions between NH and C=O functions in the polycatenar amides, FT-IR measurements at variable temperature were performed on the selected compound 4a as a representative of the amides.

The compound was heated to the isotropic liquid and the spectra, represented in the figure 6, were recorded at different temperatures corresponding to different states of the cooling process: 220 °C (liquid phase), 170 °C (columnar mesophase), 100 ° C (crystal phase). In the liquid phase, the FT-IR spectra showed NH and C=O bands at 3306  $\text{cm}^{-1}$  and 1657  $\text{cm}^{-1}$  respectively. In the mesomorphic and crystal phase, no significant shifts of these bands were observed. This indicates that hydrogen bond interactions are very strong with similar magnitude in the crystalline, mesomorphic and isotropic states. However, the FT-IR spectra of the same compound 4a, realized in solution with chloroform as solvent without hydrogen bonding features (figure 7), allowed to see a clear shift of these bands (NH and C=O bands found around 3430 and 1673 cm<sup>-1</sup> respectively), indicating a disruption of these hydrogen bond interactions in solution.



Figure 6. FT-IR spectra of 4a at different temperatures



Figure 7. FT-IR spectrum of 4a in chloroform

## **Optical properties**

## Ultraviolet-visible absorption and photoluminescence spectroscopy

Compounds incorporating benzobisthiazole units are known for their ability to show very interesting optical properties  $^{2,4\mbox{-}6,12,13,30}$ such as high fluorescence. Considering that the length of the side chains do not influence the optical properties, only solutions in dichloromethane of the amides 3a and 4a as representative compounds of the series 3 and 4, respectively, were analyzed by the ultraviolet-visible (UV-vis) spectroscopy and their absorptionemission spectra are depicted in figure 8. Similar experiments on the compounds of the series 2 could not be carried out because of their insolubility in classical organic solvents. The solution concentration used for 3a and 4a in dichloromethane are 2.6 x  $10^{-6}$ M and the photophysical data are summarized in the table 3. As observed in the esters series<sup>12</sup>, both compounds **3a** and **4a** present three absorptions with a maximum at 374 nm and two others at 358 and 391 nm. The molar extinction coefficients were determined around 1.0x10<sup>-4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> for both compounds. Concerning the emission spectra, the compounds 3a and 4a show three bands at 403, 426, 452 nm and 404, 427 and 454 nm respectively, being the two first ones with higher emissions. The emission colors of these compounds are in the violet-blue region. The presence of benzene rings in the benzobisthiazole unit in the structure of 3a and 4a explains the absorption bands through spin-allowed  $\pi$ - $\pi^*$ transitions. Moreover, the molecular structure presents surely a high electronic  $\pi$ -delocalization, as stated by the high values observed for the molar extinction coefficients. Compared to the esters series<sup>12</sup>, the values of the absorption or emission bands are higher due to a favored planar geometry originated by the electronic delocalization in the amide groups. The photoluminescence quantum yield  $\Phi_{\text{PL}}$  for each sample was determined by comparison with a well-known reference compound

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(9, 10-diphenylantracene in cyclohexane,  $\Phi_r$ =0.950). The general equation used for the determination of the relative quantum yield is given as follows:

$$\Phi_{\rm PL} = \Phi_{\rm r} X \left( \frac{\rm Abs_{reference}}{\rm Abs_{sample}} \right) X \left( \frac{\rm A_{sample}}{\rm A_{reference}} \right) X \left( \frac{\eta_{\rm sample}^2}{\eta_{\rm reference}^2} \right)$$

where  $\Phi_r$  is the photoluminescence quantum yield of the reference compound 9, 10-diphenylantracene; Abs<sub>reference</sub> and Abs<sub>sample</sub> are the absorbances of the reference and the sample, respectively; A<sub>sample</sub> and  $A_{reference}$  are the integrated areas of the emission peak of the sample and the reference, respectively;  $\eta_{sample}$  and  $\eta_{reference}$  are the refractive indices of the sample and reference solutions in dichloromethane (pure solvents were supposed) respectively. The photoluminescence quantum efficiencies of **3a** and **4a** in dichloromethane solution were 0.28 y 0.33 respectively, lower than those observed for the similar ester compounds. This result can be explained by a higher molecular interaction in the amides series, disfavoring the luminescence property.



**Figure 8.** Absorption and emission spectra of compounds **3a** and **4a**.

Comp.	$\lambda_{abs, max}$	λ <sub>em.max</sub>	ε		

Comp.	۸ <sub>abs. max</sub> (nm) <sup>a</sup>	Λ <sub>em.max</sub> (nm) <sup>b</sup>	د (L mol <sup>-1</sup> cm <sup>-1</sup> )	Stokes shift (nm)	$\boldsymbol{\Psi}_{PL}$
3a	358, 374, 391	403, 426, 452	$1.04 \times 10^{4}$	45, 52, 61	0.28
4a	358, 374, 391	404, 427, 454	$1.05 \times 10^{4}$	46, 53, 63	0.33

<sup>a</sup> Measured in dichloromethane solutions (2.6 x  $10^{-6}$  M)

<sup>b</sup> Excited at absorption maximum

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<sup>c</sup> Quantum yield in dichloromethane solutions relative to 9,10-diphenylanthracene ( $\Phi_{std}$  = 0.95 in cyclohexane solution)

#### Solid-state fluorescence emission

Fluorescence emission spectra in solid state were obtained in a confocal fluorescence microscope equipped with a spectral detector and using of 405 nm laser as excitation source. Compound **4c** was used as a representative molecule of the amide series. Figure 9 shows the comparison of the emission spectra obtained in solid state and in solution for compound **4c**. A bathochromic shift was observed in the emission spectra in solid state as compared with the one in solution. This shift could be explained by the intermolecular interactions present in the solid state. Indeed, an overlapping of molecular orbitals between molecules is generated in the solid state, leading to a decrease in the energy gap of the excited state and the shift of the emission to higher wavelengths.



Figure 9. Emission spectra of 4c in solution and solid state.

Nowadays, a considerable interest is focused on supramolecular systems with fluorescent properties which can be modified by external sources<sup>15,41-43</sup> such as ions, molecules or light. Since the amide groups can be protonated in acid environment, a study on protonation for the compounds belonging to series **3** and **4** was performed. Film samples of these compounds were exposed to ultra-violet radiation of 365 nm and a green-blue emission color was observed (figure 10a). These materials treated with drops of acetic acid (HAc) showed yellow emission color (figure 10b), using the same ultra-violet radiation. This process is completely reversible: the same acidified film, once neutralized by a base as ammonia solution, exhibited a green-blue color emission. Because of their high melting point and tendency to decomposition, the amides of series **2** were not submitted to this study.

Solid state spectra of the compounds shown in figure 10 were taken under the microscope using a 405 nm excitation laser. The emission spectra from neutral film corresponding to **4c** (Figure 10, table 4) showed an emission maximum at 476 nm and the acidified film of **4c-HAc** (Figure 10, table 4) at 582 nm, explaining the dramatic color change observed in the visual inspection shown in Figure 10a and 10b. This type of molecules shows areas with different electronic density. The benzobisthiazole and amide groups show low electronic density (denominated *acceptors*, A) and the lateral benzene rings together with the alkoxy chains show high electronic

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density (denominated *acceptors*, B). These types of A-B systems are characterized by a photo-inducible fluorescence as a result of intramolecular charge transfer (ICT) in the excited state. In these systems, when the sample is acidified, protonation of the oxygen in the amide groups would occur since this is the most basic area of the molecule, generating areas with higher electron acceptor power when compared with the neutral molecules. Even more, a system with larger electronic delocalization is generated (Figure 11), favoring the intramolecular charge transference and stabilization of the excited state with the resulting change in fluorescence color<sup>44</sup>.



**Figure 10.** Left side: Pictures corresponding to a film of compound **4c** exposed to ultra-violet radiation of 365 nm: a) neutral film and b) film acidified by acetic acid. Right side: solid state fluorescence spectra of the films, determined from a spectral image.

Table 4. Photophysical properties in solid state of 4a.

Compounds	$\lambda_{em. max}$ (nm)	Emission colour
4c <sub>(neutral film)</sub>	476	Blue
4c-HAc <sub>(acidified film)</sub>	582	yellow



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Figure 11. Scheme representing the protonation of the amide compounds and the electronic delocalization.

## Gel formation and fluorescence analysis

The products from the series **2** and **3** did not show ability to be potential gelators, because of their very low solubility in classical organic solvents. Among the three compounds of series **4**, only product **4c**, presenting the largest side chains, showed the ability to form a stable gel in organic solvents as chloroform and tetrahydrofuran THF, at concentrations lower than 5 %, as appreciated in figure 12 (a, b, c, d).

Table 5 shows the maximum solvent retention of compound 4c. As indicated in this table, this compound was able to form a stable gel in chloroform with a concentration of 0.8% in weight whereas in THF the stable gel formation was observed for a concentration of 1.5% in weight (Figure 12 a and b). The large solvent retention capacity in chloroform allows to class this compound as a supergelator substance, which is able to form a gel with concentrations less than 1% in weight.

#### Table 5. Gel capacity of 4c versus concentration in weight

4c	5%	2.5%	1.5%	1%	0.8%	0.5%	
CHCl <sub>3</sub>	G	G	G	G	G	S	
THF	G	G	G	S	S	S	
S: soluble, G: gel.							

Since organogels with luminescent properties could be destined to potential applications as optical sensors, the fluorescence properties of the gel formed with 0.8% of compound **4c** was studied. The UV illumination of the gel produced blue fluorescence (Figure 12c) confirmed by the emission spectra (Figure 12d) obtained from the gel using a confocal microscope equipped with a spectral detector (see methods<sup>29</sup>).

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**Figure 12.** Formation of a fluorescent gel from compound **4c**; (a) Gel formation at 1.5% of compound **4c** in THF; (b) Gel formation at 0.8% of compound **4c** in chloroform; (c) Photograph under illumination with a UV lamp of the gel obtained at 0.8% of compound **4c** in chloroform; (d) solid state emission spectra for the gel obtained at 0.8% of compound **4c** in chloroform.

The morphology of the xerogels of compound **4c** was studied by scanning electron microscopy (SEM). Figure 13 shows the SEM images of the xerogel **4c** obtained after elimination of chloroform and THF respectively. In the pictures with 500x magnification, a lamellar morphology can be distinguished, whereas with 1500x magnification, it is possible to observe typical fibrillar morphologies for both gels, with a diameter of 250 nm for the gel in chloroform and 180 nm for the gel in THF. From these images, it can be concluded that there is a supramolecular self-organization that follows a hierarchical order. First, gelling molecules self-organize into microfibers which are incorporated in fibrillar networks. Finally, these network structures are organized in lamellar systems.



**Figure 13.** SEM micrographs of xerogel **4c** obtained after elimination of chloroform (a) or THF (b), with magnification 500x and 1500x.

## Conclusions

In spite of the complex molecular structure of the polycatenar BBZT amide compounds designed for achieving liquid crystal and gel properties, the synthetic route proposed in this investigation can be considered as a remarkable success from the point of view of great yields and mild reaction conditions. The photoluminescent behavior in solution or solid state of the BBZT unit incorporated in such large molecules was kept and confirmed by optical studies showing good fluorescence quantum yields in organic solvents. Even if the amide functions did not allow to increase the optical properties because of the hydrogen bond formation, their presence results to be an excellent way to achieve a very attractive property concerning the color change if acids or bases are added. Among the polycatenar compounds synthesized in this investigation, the hexacatenar molecules represent the series which showed the most adequate structural characteristics for obtaining liquid crystal and organogel properties. Indeed, as reported and stated for other liquid crystal materials, the number, positions and lengths of the side chains in this kind of molecules are crucial factors to target the corresponding properties. As expected, Colh mesomorphism was generated and determined from the analysis performed by POM, DSC and XRD techniques, leading to very promising results for electronic transport applications in such molecular structure composed by benzene rings, BBZT unit and amide function. In the case of gel materials, a remarkable result was found with the hexacatenar BBZT compound containing alkoxy chains of 14 carbons, able to behave as a super-gelator in chloroform. By electronic microscopy a microfiber structure is observed for the corresponding xerogel, which is organized in an extremely intertwined network, caused by a complex supramolecular assembly. One would assume that the fluorescence properties of the BBZT unit present in such sophisticated structure could be quenched. However the optical studies showed that this property was maintained, allowing to achieve a very attractive super-gel with blue colour emission. This result implies that the molecular organization in this gel material is highly ordered due to the molecular interactions mentioned previously, avoiding a turned off effect of the fluorescence.

The information obtained in this investigation delivers us very important chemical keys for the design and preparation of hybrid fluorescent materials with liquid crystal and gel-forming properties. The very promising results encourage us to study the chemical modifications of these polycatenar BBZT compounds changing the side chains which are the most determinant factors implied in the liquid crystal and gel potentialities. Since main investigation efforts aim to the formation of solid-state blue emitters due to their scarcity, the incorporation of BBZT unit in adequate organic systems could be a very attractive alternative way to achieve such materials, as investigated and described in this paper.

Finally, additional promising applications of these materials should be oriented to the fabrication of optical chemical pH sensors.

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