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Article

## Liquid Crystalline Ionic Dendrimers Containing Luminescent Oxadiazole Moieties

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**Supporting Information** 

**ABSTRACT:** Two novel series of dendrimers constituted by the ionic grafting of poly(propyleneimine) PPI- $(NH_2)_x$  (x = 4, 8, 16, 32, 64) and poly(amidoamine) PAMAM- $(NH_2)_x$  (x =64) with carboxylic acids bearing an oxadiazole ring have been synthesized, and their liquid crystalline properties have been investigated. Series I is generated by the ionic attachment between the dendrimers and 1,3,4-oxadiazole-containing acids. Series II results from the ionic junction of the dendrimers to 1,2,4-oxadiazole-containing acids. The liquid crystalline behavior has been investigated by means of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffractometry (XRD). The liquid crystal



properties are significantly improved in the dendrimers compared to the mesogenic precursors. The structural parameters determined by X-ray diffraction reflect the different supramolecular organization built by each kind of oxadiazole-containing acid introduced. On the basis of these experimental results, a packing model is proposed based on a microsegregation phenomenon and a variable degree of interdigitation between the mesogenic units. The absorption and emission properties of the compounds have also been studied. To our knowledge, these are the first dendrimers reported up to date combining oxadiazole units and liquid crystal properties.

## ■ INTRODUCTION

Dendrimers are highly branched macromolecules that have attracted significant interest in material science and biomedicine fields.<sup>1</sup> Their unique architecture originates novel properties, such as better solubility and lower viscosity than their analogous linear polymers. Moreover, the high density of functional groups contained in their structure allows the introduction of a higher number of active units with specific properties.

The 1,3,4- and 1,2,4-oxadiazole moieties have been incorporated to many series of organic compounds due to their interest as electron transporting materials or their application in emission layers for OLEDS<sup>2</sup> and in biology.<sup>3</sup> These molecules have also been investigated in the liquid crystal field. As a general term, they tend to generate mesophases typical of rodlike mesogens such as the smectic or the nematic phase,<sup>4</sup> but some columnar mesophases<sup>5</sup> have also been described when these molecules are conveniently designed to possess a disk shape.

More interesting is the occurrence of the biaxial nematic mesophase for some of these derivatives.<sup>6</sup> This mesophase, of great interest in liquid-crystal electro-optical display technology, has also been investigated in dendrimers. Thus, the side-on attachment of the mesogen as a side group to siloxane dendrimers hinders the rotation about the molecular long axis, and this has been demonstrated to be a good strategy to avoid the rotational symmetry in the molecule and to give a biaxial nematic mesophase.<sup>7</sup>

Oxadiazole units have been extensively incorporated in dendrons<sup>8</sup> and dendrimers<sup>9</sup> to study their luminescent properties in nonmesomorphic materials. The highly branched structure of the dendrimer may improve the luminescence efficiency of the materials in films since their globular shape reduces intermolecular interactions.<sup>10</sup> Interestingly, light harvesting effects have also been observed in luminescent dendrimers.<sup>11</sup> However, no works concerning the liquid crystalline behavior of dendrimers bearing oxadiazole have been reported. The well-defined architecture of dendrimers enables for the specific and controlled location of the oxadiazole moieties in the dendritic scaffold, and this feature favors the supramolecular organization required to obtain mesomorphic properties.

A simple method to obtain mesomorphic dendrimers is the incorporation of appropriate molecules to the periphery of a dendrimer.<sup>12</sup> Although most of the works collected up to now deal with covalent attachment, the ionic junction of molecules

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bearing a carboxylic group to the amine terminal groups of the poly(propyleneimine) (PPI) and poly(amidoamine) (PAMAM) dendrimers has demonstrated to be an easy and versatile strategy to produce mesomorphic materials.<sup>13</sup>

Following this approach, we have prepared the two series of dendrimers shown in Scheme 1. Series I is constituted by

# Scheme 1. Schematic Representation and Nomenclature of the Reported Dendrimers



dendrimers coming from the ionic functionalization of PPI (x =4, 8, 16, 32, and 64) and PAMAM (x = 64) with carboxylic acids  $(1,3,4-\text{OXA}_n)$  bearing the 1,3,4-oxadiazole moiety with different spacer lengths (n = 4 and 10). One dendrimer coming from the covalent attachment of the 1,3,4-OXA10 unit to the third-generation PPI (x = 16) is also included in this series. Series II is formed by ionic dendrimers constituted by the functionalization of PPI (x = 16 and 64) with carboxylic acids  $(1,2,4-OXA_n)$  containing the 1,2,4-oxadiazole ring with different spacer length (n = 4 and 10). Both dendritic scaffolds have been chosen because of their easy functionalization by means of the transfer proton reaction between their peripheral amine groups and the carboxylic acid. Besides, most of the compounds have been prepared by using the PPI dendrimer because this dendrimer presents higher fluidity and thermal stability when compared with the PAMAM core. These two properties are of great importance for future applications of these materials.

The aim of this work is to study the liquid crystalline behavior, looking for the nematic biaxial mesophase, and to evaluate the luminescent properties in these dendrimers.

#### EXPERIMENTAL SECTION

**1. Materials and Methods.** PPI- $(NH_2)_x$  (x = 4, 8, 16, 32, and 64) dendrimers were purchased from SyMO-Chem BV (Eindhoven, The Netherlands), and Starburst-PAMAM- $(NH_2)_{64}$  dendrimer was manufactured by Dendritech. The rest of reagents were purchased from Aldrich, and all of them were used as received. Anhydrous THF used for dendrimer preparation was purchased from Scharlau and dried using a solvent purification system.

The infrared spectra of all the compounds were obtained with a Nicolet Avatar 360 FTIR spectrophotometer in the 400–4000 cm<sup>-1</sup> spectral range using KBr pellets and NaCl cells. <sup>1</sup>H NMR was performed on a Bruker AVANCE 400 spectrometer and on a Bruker AVANCE 300 spectrometer. <sup>13</sup>C NMR was performed on a Bruker AVANCE 400 spectrometer operating at 100 MHz and on a Bruker AVANCE 300 spectrometer operating at 75 MHz. Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer.

Mesogenic behavior and transition temperatures were determined using an Olympus DP12 polarizing optical microscope equipped with a Linkam TMS91 hot stage and a CS196 central processor.

Differential scanning calorimetry (DSC) experiments were performed in DSC TA Instruments Q-20 and Q-2000 equipments. Samples were sealed in aluminum pans, and a scanning rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere was used. The equipment was calibrated with indium (156.6 °C, 28.4 J g<sup>-1</sup>) as the standard. Three thermal cycles were carried out. The mesophase transition temperatures were read at the maximum of the corresponding peaks. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q5000 at a rate of 10 °C min<sup>-1</sup> under an argon atmosphere.

The XRD experiments were performed in a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu K $\alpha$  beam. Lindemann glass capillaries with 0.9 mm diameter were used to contain the sample, and when necessary, a variable-temperature attachment was used to heat the sample. The patterns were collected on flat photographic film perpendicular to the X-ray beam. Bragg's law was used to obtain the spacing.

UV-vis absorption spectra were measured with a UV4-200 from ATI-Unicam using  $10^{-5}$ - $10^{-6}$  M solutions in CHCl<sub>3</sub> (HPLC grade). Fluorescence spectra were measured with a Perkin-Elmer LS50B fluorescence spectrometer using solutions in CHCl<sub>3</sub> of ca. 0.01 absorbance (about  $10^{-8}$ - $10^{-9}$  M) under excitation at the absorption maximum. Films were prepared by casting of a solution of ~1 mg/mL in CHCl<sub>3</sub> on a quartz plate.

#### 2. Synthesis and Nomenclature.

2.1. Oxadiazole Acids. Carboxylic acids based on two oxadiazole isomers (1,3,4- and 1,2,4-) have been used to prepare the dendrimers. They are denoted 1,3,4-OXA<sub>n</sub> and 1,2,4-OXA<sub>n</sub>. The subscript "n" indicates the length of the spacer between the rigid moiety and the carboxyl group, namely n = 4 and 10. The synthesis of 1,3,4-OXA<sub>n</sub> and 1,2,4-OXA<sub>n</sub> was performed following previously described methods (Scheme 2).<sup>6d,14</sup>

2.2. Ionic Dendrimers. Ionic dendrimers were synthesized by a procedure previously described by us,<sup>13c</sup> following the method of Crooks<sup>15</sup> as schematically represented in Scheme 3a. Namely, x equiv of the OXA<sub>n</sub> acid was dissolved in anhydrous THF. The mixture was added to a solution of 1 equiv of PPI or PAMAM dendrimer of the corresponding generation (PPI-(NH<sub>2</sub>)<sub>x</sub> or PAMAM-(NH<sub>2</sub>)<sub>x</sub>) in anhydrous tetrahydrofuran (THF) and sonicated for 10 min. The mixture was then slowly evaporated at room temperature and dried in vacuum until the weight remains constant for ca. 12 h at 40 °C. These compounds are named D-(1,3,4-OXA<sub>n</sub>)<sub>x</sub> or D-(1,2,4-OXA<sub>n</sub>)<sub>x</sub>, where D denotes the type of dendrimer matrix (PPI or PAMAM), *n* the spacer length of the acid, and *x* the number of terminal amine groups of the dendrimers (related to the generation). The terminal chain of the oxadiazole-based carboxylic acids is pentyl in all cases.

2.3. Covalent Dendrimer. Covalent dendrimer (PPI- $(1,3,4-OXA_{10})_{16}$ -cov) belonging to series I was synthesized following a method previously described,<sup>16</sup> as schematically represented in Scheme 3b. 1.03 equiv of 1,3,4-OXA<sub>10</sub> acid was dissolved in THF

Scheme 2. Synthetic Route and Nomenclature of Intermediates for 1,3,4-OXA<sub>n</sub> and 1,2,4-OXA<sub>n</sub> Acids



(10 mL), and a solution of carbonyldiimidazole (CDI) (1 equiv) in THF (10 mL) was slowly added to the acid solution. The reaction mixture was stirred for 1 h at room temperature under a stream of argon to remove the  $CO_2$  formed. The mixture was transferred to a Schlenk flask containing the PPI (1 equiv of terminal amino groups). The mixture was heated to 40 °C for 72 h. The solvent was half reduced in vacuum, and then 50 mL of water was added to yield a precipitate, which was isolated by filtration. The product obtained was purified by further washing with water and hot methanol to give a white power after drying in vacuum (51% yield).

#### RESULTS AND DISCUSSION

**1.** Characterization of the Dendrimers. IR and NMR spectroscopy, together with elemental analysis, reveal the correct formation of the dendrimers (series I and II) and

their purity. MALDI-TOF spectrometry was also employed to characterize the covalent dendrimer, but the ionic nature of the rest of the dendrimers prevents the use of this technique.

1.1. FT-IR Characterization. As observed in Figure 1a, the stretching absorption at  $1707-1699 \text{ cm}^{-1}$  corresponding to the carbonyl groups of 1,3,4-OXA<sub>n</sub> acids is replaced by a new band corresponding to the asymmetric stretching absorption of the carboxylate group at  $1560-1550 \text{ cm}^{-1}$  in ionic dendrimers of series I. In the case of dendrimers of series II, the band of the carbonyl group shifts from 1707 to 1705 cm<sup>-1</sup> in the 1,2,4-OXA<sub>n</sub> acids to  $1567-1561 \text{ cm}^{-1}$  in the carboxylate of the ionic dendrimers (see Figure 1a).<sup>17</sup> For PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>-cov a band at 1641 cm<sup>-1</sup> corresponding to the symmetric stretching of the carbonyl group in the amide bond replaces the band of



Scheme 3. Schematic Representation of the (a) Ionic Synthetic Route and (b) Covalent Synthetic Route of the Dendrimers

Figure 1. FT-IR spectra: (a) PPI-(1,2,4-OXA<sub>10</sub>)<sub>16</sub> (green), 1,2,4-OXA<sub>10</sub> (red), PPI<sub>16</sub> (black); (b) PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>-cov (blue), 1,3,4-OXA<sub>10</sub> (red), PPI<sub>16</sub> (black).



**Figure 2.** (a) <sup>1</sup>H NMR spectra of PPI- $(1,3,4-OXA_{10})_{16}$ -cov (blue), PPI<sub>16</sub> (black), and PPI- $(1,3,4-OXA_{10})_{16}$  (red). (b) <sup>13</sup>C NMR spectra of PPI- $(1,3,4-OXA_{10})_{16}$ -cov (blue), 1,3,4-OXA<sub>10</sub> (black), and PPI- $(1,3,4-OXA_{10})_{16}$  (red).

the carboxyl group in the 1,3,4-OXA<sub>10</sub> acid at 1707 cm<sup>-1</sup> (see Figure 1b). Moreover, a band at 3295 cm<sup>-1</sup> corroborates the presence of the amide NH group.

1.2. NMR Experiments. Dendrimers were studied by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. In <sup>1</sup>H NMR experiments (Figure 2a) the absence of signal at 2.70 ppm related to  $[-C\underline{H}_2-NH_2]$  of PPI and the appearance of another signal at ca. 2.90 ppm corresponding to  $[-C\underline{H}_2-NH_3^+]$  for ionic PPI-

 $[1,3,4-\text{OXA}_n]_x$  and PPI- $[1,2,4-\text{OXA}_n]_x$  compounds (series I and II) reveals the complete formation of the salts in the ionic compounds. In the same way, the shift of the signal from 3.30 p p m  $[-\text{NHC}\underline{H}_2\text{CH}_2\text{NH}_2]$  to ca. 3.45 p p m  $[-\text{NHC}\underline{H}_2\text{CH}_2\text{NH}_3^+]$  and the displacement from 2.70 ppm  $[\text{NHCH}_2\text{C}\underline{H}_2\text{NH}_2]$  to ca. 3.05 ppm  $[\text{NHCH}_2\text{C}\underline{H}_2\text{NH}_3^+]$  indicates the salt formation in PAMAM derivatives (not shown). In the covalent compound  $(\text{PPI-}[1,3,4-\text{OXA}_{10}]_{16}^-$ 

cov) the signal is shifted from 2.70 to 3.30 ppm, which indicates the formation of the amide bond  $[-C\underline{H}_2-NHCO]$  (Figure 2a).

In the <sup>13</sup>C NMR spectra (Figure 2b) the signal of the carbon atom of the carboxyl group (COOH) of the acid shifts from 178.2 ppm (1,3,4-OXA<sub>10</sub>) to 179.2 ppm (PPI-(1,3,4- $OXA_{10})_{16}$ ), which indicates the formation of the carboxylate (COO<sup>-</sup>). Likewise, the deprotonation of the carboxylic acid is corroborated by the displacement of the signal corresponding to the  $C_{\alpha}$  to the carbonyl group (<u>CH</u><sub>2</sub>-COOH) from 33.8 ppm in the acid to 36.9 ppm in the dendrimer  $(CH_2-COO^{-})$ . Carboxylate is also formed in the case of PAMAM dendrimers, as denoted by the signal shift from 178.2 ppm (in case of the 1,3,4-OXA10 acid) to 179.5 ppm (asigned to the carboxylate group in PAMAM- $(1,3,4-OXA_{10})_{64}$  (not shown). The formation of the amide group in the case of PPI-(1,3,4- $OXA_{10})_{16}$ -cov is confirmed by the appearance of the signal at 173.6 ppm, assigned to the carbon of the amide group (CH<sub>2</sub>NHCO) (see Figure 2b).

1.3. MALDI-TOF Analysis. The complete functionalization of PPI- $(1,3,4-OXA_{10})_{16}$ -cov was checked by MALDI-TOF mass spectrometry. The MALDI-TOF MS spectrum reveals the presence of an intense peak corresponding to the fully functionalized dendrimer (see Figure S1, Supporting Information). Except for the peak appearing at 9925 that could correspond to the dendrimer with one nonfunctionalized amino group, the rest of the peaks must be associated with statistical defects present in the original PPI dendrimer.<sup>18</sup>

**2. Thermal Stability of the Dendrimers.** The thermal stability of the dendrimers was studied by TGA experiments (see Table S1, Supporting Information).

The type of OXA moiety (1,3,4- or 1,2,4-) and the length of the spacer in the OXA<sub>n</sub> moiety (n = 4, 10) exercise a marked influence in the onset temperature of decomposition of these dendrimers. Thus, dendrimers bearing the 1,3,4-OXA<sub>n</sub> moiety possess the onset temperature of decomposition above 340 °C, whereas those containing the 1,2,4-OXA<sub>n</sub> moiety exhibit lower temperatures (between 275 and 305 °C). Likewise, when comparing dendrimers with the same OXA<sub>n</sub> moiety, it is observed that temperatures of decomposition for the longer spacer (n = 10) compounds are at least 15 °C higher than those bearing the shorter spacer (n = 4).

The type of bond affects the thermal stability of the compounds. Hence, the temperature at which 5% of initial mass is lost  $(T_{5\%})$  is higher for the covalent compound (PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>-cov) when compared with its homologous ionic compound (PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>) and the rest of the compounds (see Table S1).

Also, the dendrimer scaffold exerts influence in the  $T_{5\%}$ , this temperature being considerably higher for PPI than for PAMAM derivatives. In fact, PAMAM dendrimers are well-known to be less thermally stable than PPI dendrimers.<sup>19</sup>

**3. Liquid Crystal Properties.** The mesomorphic behavior of the compounds was analyzed by POM, DSC, and X-ray diffraction. Three cycles were carried out in DSC experiments, and data were taken from the second cycle. In some cases, the isotropization temperatures were taken from POM observations because no transition peaks were detected in the DSC curves.

3.1. Liquid Crystal Properties of the Precursors. The type of oxadiazole moiety plays a determinant role in the liquid crystal behavior of the precursors. Indeed, precursors of series I containing the 1,3,4-oxadiazole ring are not mesomorphic or the mesomorphism is only monotropic, whereas those

belonging to series II (precursors of 1,2,4-OXA<sub>n</sub>) exhibit enantiotropic mesomorphism (see Table 1 and Table S2).

## Table 1. Temperatures and Enthalpies of Selected Precursors $^{a}$

series	compound	thermal data
Ι	3	C 197 C' 205 [20.1] I
Ι	1,3,4-OXA <sub>4</sub>	C 186 [54.0] I; I 166 <sup>b</sup> N 162 [50.4] C
Ι	1,3,4-OXA <sub>10</sub>	C 175 [47.9] I
II	10	C 120 [0.6] C' 154 [20.8] SmA <sup>c</sup> N 217 [0.6] I
II	1,2,4-OXA <sub>4</sub>	C 153 [26.7] SmA 190 [0.5] N 217 [1.0] I
II	1,2,4-OXA <sub>10</sub>	C 142 [35.3] SmA 181 [0.7] N 193 [0.8] I

<sup>*a*</sup>Temperatures (°C) at the maximum of the peak and enthalpy values (kJ mol<sup>-1</sup> in brackets) of the transitions obtained by DSC in the second heating process, or in the second cooling process in the case of the monotropic mesophases, performed at 10 °C/min. C, C' = crystalline phases, SmA = smectic A mesophase, N = nematic mesophase, I = isotropic liquid. <sup>*b*</sup>Thermal transition observed only by POM. <sup>*c*</sup>The SmA-N transition is hidden in the C'-SmA transition.

3.2. Liquid Crystal Properties of the Dendrimers. In spite of the absence of mesomorphism or the occurrence of only monotropic behavior in some  $OXA_n$  acids, all dendrimers exhibit liquid crystalline properties in addition to a number of crystal-to-crystal transitions (Table 2).

The liquid crystalline temperature ranges oscillate between 30 and 50  $^{\circ}$ C, being slightly higher for PAMAM derivatives when compared with their PPI homologues. This fact may be connected with the different nature of the dendrimer scaffolds because of the existence of hydrogen bonds in the structure of the PAMAM core.

The covalent dendrimer (PPI- $(1,3,4-OXA_{10})_{16}$ -cov) presents a shorter mesomorphic range than its homologous ionic compound (PPI- $(1,3,4-OXA_{10})_{16}$ ). Thus, the ionic attachment enhances the tendency of these compounds to display liquid crystal properties, a feature that is in good agreement with other reported works.<sup>20</sup>

Dendrimers belonging to series I display higher melting and isotropization temperatures when bearing the shorter spacer (n = 4). This is probably due to the increase in the interactions between the promesogenic moieties compared to the longer spacer (n = 10).

Compounds of series II exhibit lower melting but higher isotropization temperatures than their homologues belonging to series I, thus presenting broader mesomorphic temperature range (between 145 and 180 °C).

On the other hand, the generation of the dendrimer does not produce remarkable influence in the melting and isotropization temperatures of the compounds belonging to both series.

All of the compounds present smectic A mesomorphism as revealed by the textures observed by POM (see Figure 3) and confirmed by the patterns obtained by XRD (vide infra). A hexagonal columnar mesophase has also been detected by XRD for PPI- $(1,3,4-OXA_{10})_{64}$  and PPI- $(1,3,4-OXA_4)_{64}$  at lower temperatures. The occurrence of this type of mesomorphism can be explained by the sterical hindrance at the periphery of the fifth generation of the PPI dendrimer. In contrast, PAMAM dendrimers show no columnar mesomorphism due to the larger volume of the PAMAM dendritic architecture with respect to the PPI one, which prevents this congestion.<sup>13c,21</sup>

**4. X-ray Studies of the Compounds.** The mesomorphic behavior of the dendrimers and precursors has been confirmed

PPI-(1,2,4-OXA<sub>4</sub>)<sub>16</sub>

PPI-(1,2,4-OXA<sub>4</sub>)<sub>64</sub>

Π

Π

SmA  $237^d$ 

SmA 240<sup>d</sup>

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series	compound			thermal data		
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>4</sub>	C 110 [4.7]	C' 130	C" 137 [27.4] <sup>c</sup>		SmA 164 [9.4]
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>8</sub>	C 98 [18.2]	C' 122	C" 130 [46.1] <sup>c</sup>		SmA 163 [37.0]
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>16</sub>	C 92 [31.2]	C' 128 [162.2]			SmA 176 [55.2]
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>16</sub> -cov	C 109 [37.3]	C' 146 [248.8]			SmA 189 [59.5]
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>32</sub>	C 91 [66.6]	C' 131 [343.3]			SmA 185 [117.5]
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>64</sub>	C 91 [114.9]	C′ 124	C" 133 [45.2] <sup>c</sup>	Col <sub>h</sub> 140 <sup>c</sup>	SmA 175 [180.6]
Ι	PAMAM-(1,3,4-OXA <sub>10</sub> ) <sub>64</sub>	C 83 [87.3]	C' 125 [429.2]			SmA 176 [390.6]
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>4</sub>	C 121 [12.6]	C' 140 [0.2]	C" 156 [1.3]		SmA 183 [6.3]
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>8</sub>	C 111 [9.0]	C' 148 [17.6]			SmA 184 [15.7]
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>16</sub>	C 110 [15.7]	C' 151 [29.0]			SmA 190 [27.5]
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>32</sub>	C 94 [60.7]	C'149 [88.7]			SmA 183 [60.4]
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>64</sub>	C 123 [76.8]			$Col_h 170^c$	SmA 190 <sup>d</sup>
Ι	PAMAM-(1,3,4-OXA <sub>4</sub> ) <sub>64</sub>	C 121 [187.6]				SmA 191 [103.4]
II	PPI-(1,2,4-OXA <sub>10</sub> ) <sub>16</sub>	C 43 [57.7]	C' 67	C"83 [69.2] <sup>c</sup>		SmA $234^d$
П	$PPI-(1.2.4-OXA_{10})$	C 65 [9.1]	C' 95 [365.1]			$SmA 240^d$

Table 2. Temperatures and Enthalpies of the Phase Transition of the Dendrimers<sup>a</sup>

C 65 [108.9]

C 59 [386.7]

<sup>*a*</sup>Temperatures (°C) read at the maximum of the corresponding peaks and enthalpy values (kJ mol<sup>-1</sup>, in brackets) of the transitions obtained by DSC corresponding to the second heating process performed at 10° C/min. The peaks are broad and transitions span several degrees below and above the peak maximum. <sup>*b*</sup>Two peaks are observed for this transition that probably correspond to overlapped melting of two crystalline phases (C' and C''). <sup>*c*</sup>Mesophase and transition temperature identified by XRD. <sup>*d*</sup>Temperature determined by POM. C, C', C''= crystalline phases, SmA = smectic A mesophase, Col<sub>h</sub> = hexagonal columnar mesophase, I = isotropic liquid.



**Figure 3.** POM textures of (a) PPI- $(1,3,4-OXA_{10})_{32}$  at 150 °C in the second heating process in the SmA phase, (b) PPI- $(1,3,4-OXA_{10})_{16}$ -cov at 140 °C in the first cooling process in the SmA phase, (c) PPI- $(1,3,4-OXA_4)_4$  at 165 °C in the second heating process in the SmA phase, and (d) PPI- $(1,2,4-OXA_4)_{64}$  at 170 °C in the first cooling process in the SmA phase.

by X-ray diffraction. Precursors exhibiting nematic mesomorphism contain a diffuse scattering maximum at low angles and a diffuse halo at high angles corresponding to the intermolecular short-range interactions between molecules. The high-angle scattering corresponds to a mean distance of 4.5–4.6 Å and is related to the mean distance between the conformationally disordered alkyl chains and between aromatic segments. The low-angle scattering arises from the short-range interaction along the main molecular axes. In the SmA mesophase (precursors of series II), this low angle scattering is replaced by a sharp, strong peak corresponding to the layer periodicity. All of the dendrimers display SmA mesomorphism. In this case, X-ray diffraction patterns are constituted by a diffuse halo in the wide angle region, corresponding to the short-range correlations between the mesogenic units and the conformationally disordered terminal chains coming from the oxadiazole moieties and from the dendrimer branches, and by one or two sharp maxima in the small angle region (see Figure S4a,b). These sharp maxima evidence a long-range lamellar packing of molecules, and when there are two small-angle maxima, they correspond to the first and second layer orders. The layer spacing of the SmA mesophase of each dendrimer was obtained by applying Bragg's law, and they are collected in Table 3.

Table 3. X-ray Structural Parameters Data of Dendrimers and 1,2,4-OXA<sub>n</sub> Acids

series	compound	$T/^{\circ}C$	phase <sup>a</sup>	structural parameters <sup><i>t</i></sup>
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>4</sub>	170	SmA	d = 42.9
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>8</sub>	165	SmA	d = 43.9
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>16</sub>	163	SmA	d = 44.8
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>16</sub> -cov	160	SmA	d = 47.4
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>32</sub>	161	SmA	d = 45.9
Ι	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>64</sub>	130	Colh	a = 49.4
	PPI-(1,3,4-OXA <sub>10</sub> ) <sub>64</sub>	150	SmA	d = 49.3
Ι	PAMAM-(1,3,4-OXA <sub>10</sub> ) <sub>64</sub>	148	SmA	d = 56.0
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>4</sub>	175	SmA	d = 56.0
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>8</sub>	168	SmA	d = 54.1
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>16</sub>	168	SmA	d = 55.4
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>32</sub>	168	SmA	d = 56.1
Ι	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>64</sub>	168	Colh	a = 67.3
	PPI-(1,3,4-OXA <sub>4</sub> ) <sub>64</sub>	180	SmA	d = 53.6
Ι	PAMAM-(1,3,4-OXA <sub>4</sub> ) <sub>64</sub>	168	SmA	d = 61.6
II	1,2,4-OXA <sub>10</sub>	175	SmA	d = 38.5
II	1,2,4-OXA <sub>4</sub>	175	SmA	d = 30.8
II	PPI-(1,2,4-OXA <sub>10</sub> ) <sub>16</sub>	165	SmA	d = 47.4
II	PPI-(1,2,4-OXA <sub>10</sub> ) <sub>64</sub>	165	SmA	d = 49.4
II	PPI-(1,2,4-OXA <sub>4</sub> ) <sub>16</sub>	170	SmA	d = 40.4
II	PPI-(1,2,4-OXA <sub>4</sub> ) <sub>64</sub>	170	SmA	d = 41.1

<sup>*a*</sup>Mesophases exhibited by the compounds at the given temperature. <sup>*b*</sup>d = layer spacing (Å) of the smectic phase. a = lattice constat of the hexagonal columnar mesophase.

The length of the low-molecular-weight molecules obtained by molecular modeling are 35.8 Å (1,3,4-OXA<sub>10</sub>), 28.7 Å (1,3,4-OXA<sub>4</sub>), 35.0 Å (1,2,4-OXA<sub>10</sub>), and 28.2 Å (1,2,4-OXA<sub>4</sub>). These data are in accordance with the experimental values obtained by XRD for the mesomorphic 1,2,4-OXA acids (38.5 Å for 1,2,4-OXA<sub>10</sub> and 30.8 Å for 1,2,4-OXA<sub>4</sub>).

It has been previously described that this kind of ionic and covalent dendrimers self-assembling in a smectic A layer adopt a cylindrical shape, in which the substitutents are statistically located upward and downward with respect to the dendrimeric core.<sup>13c,22</sup> The assumption of this location of the oxadiazole moieties in the dendrimers here described should lead to layer spacing being higher than twice the oxadiazole moieties length. However, the XRD experimental layer spacing values are significantly lower, suggesting some peculiarities in the distribution of the oxadiazole units in the cylindrical model. Furthermore, dendrimers of series I bearing the 1,3,4-OXA<sub>4</sub> unit exhibit a layer spacing of 53.6–56.1 Å, whereas dendrimers containing the same oxadiazole ring but a longer spacer (1,3,4-OXA<sub>10</sub>) possess a shorter layer spacing (42.9–49.3 Å).

The most plausible explanation to justify these unexpected experimental features is that some interdigitation of the oxadiazole moieties belonging to adjacent layers takes place (see Figure 4). In fact, the longer spacer present in the structure of 1,3,4-OXA<sub>10</sub> favors a more efficient interaction with molecules of the neighboring layers. This packing is based on a side-by-side arrangement of the aromatic moieties of adjacent molecules in a head-to-tail fashion, and this arrangement allows the electrostatic interactions between the carboxylate groups and the ammonium groups of the dendrimer (Figure 4a). On the other hand, interdigitation of 1,3,4-OXA<sub>4</sub> with a side-byside arrangement of the aromatic moieties would preclude the ionic interactions between the carboxylate groups and the ammonium as a consequence of the mismatch between the length of the different segments of the mesogenic units.

Therefore, the 1,3,4-OXA<sub>4</sub> units do not interdigitate to such a large extent, and the side-by-side arrangement of this aromatic units is probably replaced by a side-by-side arrangement of the hydrocarbon chains (Figure 4b). In both models there is segregation of the aromatic units and the hydrocarbon chains in different sublayers.

The layer thickness is also dependent on the nature of the dendrimer matrix. Greater values are obtained for the two PAMAM derivatives as it was expected due to its larger size when compared to PPI, and the same relationship as for the PPI derivatives is observed between the spacer length and the layer periodicity.

The layer thickness of the ionic PPI- $(1,3,4-OXA_{10})_{16}$  dendrimer (44.8 Å) and that of its analogous covalent PPI- $(1,3,4-OXA_{10})_{16}$ -cov (47.4 Å) dendrimer do not significantly differ from each other. The slightly higher spacing layer value obtained for the covalent one gives evidence of a higher mobility present in the case of the ionic compounds, where the moieties can fluctuate in position and slightly penetrate in the dendrimer. By contrast, in the covalent compound moieties occupy fixed positions. The same tendency has been previously described in other similar dendrimers.<sup>13a</sup> This enhanced mobility may allow the ionic compound to reach the mesomorphic state at lower temperatures than the covalent analogue.

It is important to highlight how a subtle change in the structure of the oxadiazole heterocycle, namely the 1,3,4- or 1,2,4-oxadiazole ring, produces great differences not only in the mesomorphic behavior, as described before, but also in the supramolecular packing of the dendrimers. Thus, dendrimers bearing the 1,2,4-OXA<sub>n</sub> unit (series II) also exhibit layer spacings consistent with interdigitation of the oxadiazole moieties. However, in this case, no influence of the spacer length is observed, and full interdigitation between molecules of adjacent layers occurs in all of the dendrimers, as deduced from the X-ray results. This fact clearly indicates that more effective intermolecular side-by-side interactions are taking place in case of the 1,2,4-OXA moieties, favoring their interdigitation independently of the spacer length.

The hexagonal columnar phase exhibited by PPI- $(1,3,4-OXA_{10})_{64}$  and PPI- $(1,3,4-OXA_4)_{64}$  is identified by the existence of two sharp reflections in the reciprocal ratio  $1:\sqrt{3}$  in the low angle region of the patterns (see Figure S4c). In this case the molecules adopt a disk shape where the dendrimer matrix is located in the central part and the oxadiazole moieties are disposed radially.

As observed in Table 3, the structural parameters of this columnar hexagonal mesophase considerably change in an unexpected way when going from the longer spacer moiety dendrimer (a = 49.4 Å) to the shorter one (a = 67.3 Å). This fact is mainly connected to the elongation of the dendrimer matrix along the vertical axis of the discs. By applying geometrical calculations taking into account the XRD experimental data,<sup>13c</sup> we have estimated the height (h) of the disks that constitute the columnar arrangement, being h = 34 Å for PPI-(1,3,4-OXA<sub>10</sub>)<sub>64</sub> and h = 16 Å for PPI-(1,3,4-OXA<sub>4</sub>)<sub>64</sub>. These height values indicate that the dendrimer with the longer spacer elongates twice along the vertical axis of the disk compared to the dendrimer with the smaller spacer. Hence, neighboring columns interpenetrate in a large extent in the case of the PPI-(1,3,4-OXA<sub>4</sub>)<sub>64</sub> (Figure 5a) compared to PPI-(1,3,4-OXA<sub>4</sub>)<sub>64</sub>

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Figure 4. Schematic representation of the molecular packing model of the ionic dendrimers in the SmA mesophase. (a) Interdigitated 1,3,4-OXA<sub>10</sub> moieties. (b) Partially interdigitated 1,3,4-OXA<sub>4</sub> moieties. (c) Schematic representation of the 1,3,4-OXA<sub>10</sub> and 1,3,4-OXA<sub>4</sub> acids. The thickness of each sublayer, and hence the space filled by each molecule region, is approximately proportional to its mass.



**Figure 5.** Schematic representation of the disk packing, values of the diameter *a*, and the height *h* of the dendrimer disks for (a) PPI-(1,3,4- $OXA_{4})_{64}$  and (b) PPI-(1,3,4- $OXA_{10})_{64}$  in the hexagonal columnar mesophase.

 $OXA_{10})_{64}$  (Figure 5b), and both situations fulfill the requirements for an efficient packing and space filling. It is interesting

to note that the interdigitation phenomenon between molecules in neighboring columns follows the same trend described for the low generation derivatives in the SmA phase. Both effects (dendrimer matrix elongation and interdigitation) are connected to each other and simultaneously contribute to account for the difference in the hexagonal lattice constant *a*.

**5.** Optical Properties. The UV-vis absorption and emission spectroscopic data of the OXA<sub>n</sub> acids and dendrimers of series I and series II in CHCl<sub>3</sub> and in casted films are summarized in Table S3 (Supporting Information). All compounds containing the same oxadiazole ring yielded identical absorption and emission spectra. No remarkable influence of the length of the spacer, the generation, or the type of dendrimer has been found. Thus, dendrimers with the 1,3,4-OXA<sub>n</sub> unit present the absorption maximum at 315-316 nm and dendrimers with the 1,2,4-OXA<sub>n</sub> moiety exhibit the absorption maximum at 295 nm (Figure 6). These absorption bands are asigned to  $\pi \rightarrow \pi^*$  transitions produced in the conjugated oxadiazole framework due to their high molar absorption coefficients ((4.7-3.3) × 10<sup>4</sup>).<sup>4e</sup>

All of the compounds present emission in the UV region. The emission spectra of the compounds are only dependent on the type of oxadiazole ring. Compounds belonging to series I exhibit the strongest emission maxima at 377-379 nm. Two less intense maxima are found at  $\sim 360$  and  $\sim 390$  nm.



**Figure 6.** UV absorption spectra in solution (CHCl<sub>3</sub>) (full line), emission spectra in solution (CHCl<sub>3</sub>) (dashed line), and emission spectra in film (dotted line). Red lines correspond to PPI-(1,3,4- $OXA_4$ )<sub>32</sub>, and black lines correspond to PPI-(1,2,4- $OXA_{10}$ )<sub>64</sub>.

Compounds in series II present only one maximum at 365–366 nm (see Figure 6).

The quantum yields of luminescence have been measured taking the 2-phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole as standard ( $\Phi = 0.80$ , benzene),<sup>23</sup> and they fluctuate between 0.46 and 0.74. Lower quantum yields are observed for series II, as it was expected because 1,2,4-oxadiazole molecules have been previously reported to produce lower quantum yield values compared with their 1,3,4-isomers.<sup>4e</sup> In general, in series I the quantum yields decrease as the generation increases. However, in series II, efficiency is not dependent on the generation. The covalent compound (PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>-cov) presents a lower value than the analogous ionic compound (PPI-(1,3,4-OXA<sub>10</sub>)<sub>16</sub>).

The emission in solid film has also been analyzed for these compounds by casting of a solution of  $\sim 1 \text{ mg/mL}$  in CHCl<sub>3</sub> on a quartz plate. Interestingly, as observed in Figure 6, emission bands appear broader respect to those in solution because of the stronger intermolecular interactions produced in the solid state. The Stokes shifts are remarkably higher in film than in solution.

#### CONCLUSIONS

We have successfully synthesized liquid crystal dendrimers containg the oxadiazole heterocycle in their structure (series I  $(1,3,4-OXA_n)$  and series II  $(1,2,4-OXA_n)$ ) using an easy and versatile method via ionic bonding of commercial amino-terminated PPI and PAMAM dendrimers with oxadiazole-containing carboxylic acids.

As far as we know, this is the first time that liquid crystalline properties have been described in dendrimers containing oxadiazole moieties in their structure. All of them present smectic A mesomorphism, although a hexagonal columnar mesophase has also been observed in some of the higher generation PPI dendrimers belonging to series I. No nematic mesomorphism has been achieved in any case. Dendrimers containing 1,2,4-OXA<sub>n</sub> (series II) exhibit lower melting points and broader mesomorphic temperature ranges than those of the 1,3,4-OXA<sub>n</sub> derivatives (series I) although they present lower thermal stability. Moreover, the liquid crystal properties are significantly improved in the dendrimers compared to the mesogenic precursors.

XRD studies reveal interesting structural details concerning the packing of these compounds in their mesophases. On the basis of the experimental results, some supramolecular models have been proposed. In particular, interdigitation between neighboring layers or columns is observed, the extent of which depends on the spacer length and the oxadiazole isomer. Regarding the luminescent properties, all the dendrimers display emission in solution and in the solid state. Derivatives bearing the 1,3,4-OXA<sub>n</sub> moiety present higher quantum yield values compared to their homologous containing the 1,2,4-OXA<sub>n</sub> unit.

It has been shown how the change in the oxadiazole heterocycle isomer leads to remarkable differences in the mesomorphism, structural parameters of the supramolecular organization, and luminescent properties of these dendrimers.

### ASSOCIATED CONTENT

#### **Supporting Information**

More details about the synthesis, characterization, thermal stability data, POM textures, XRD patterns, and optical data of the materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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