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# Columnar mesomorphism of bent-rod mesogens containing 1,2,4-oxadiazole rings

Hugo Gallardo [a,*], Marli Ferreira [a], André A. Vieira [a], Eduard Westphal [a], Fernando Molin [a], Juliana Eccher [b], Ivan H. Bechtold [b]

[a] Departamento de Química-INCT Catalise, Universidade Federal de Santa Catarina—UFSC, 88040-900 Florianópolis, SC, Brazil
[b] Departamento de Física, Universidade Federal de Santa Catarina—UFSC, 88040-900 Florianópolis, SC, Brazil

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ABSTRACT

In this study, the synthesis, characterization, and mesomorphic properties of ten new bent-rod compounds containing two units of 1,2,4-oxadiazoles are reported. In order to understand the relationship between the structure and the mesomorphic behavior, molecules containing a variety of polar substituents (i.e., I, $NO_2$, $NH_2$, OH) on the central rigid core were prepared. The hexagonal columnar mesomorphism was characterized by DSC and POM and the nature of the mesophases was established through XRD studies. The driving force for self-assembly can be explained by microsegregation between the aliphatic parts and the polar parts, producing a dimer, trimer, and tetramer inside a single disc.



## 1. Introduction

Discotic liquid crystals (DLCs) are of great interest due to their unique self-assembled structures and potential applications in organic devices, such as field-effect transistors,[1] photovoltaic solar cells,[2] optical data storage devices,[3] sensors,[4] and electroluminescent displays.[5] The main reason for the wide applicability of DLCs is their high charge-carrier mobility and their one-dimensional (1D) aromatic π–π stacking.[6]

DLCs are typically described as disc-shaped molecules with a rigid aromatic core and flexible peripheral chains.[7] However, many non-discoid molecules, such as half-disc shaped,[8] butterfly-shaped,[9] star-shaped,[10] and bent-core,[11] have been studied in an attempt to develop new types of core architecture for columnar mesophases. The driving forces for the self-assembly of non-discotic molecules to form a disc-like structure include hydrogen-bonding,[12] π–π interactions,[13] ionic interactions,[14] and charge-transfer.[15] Another driving force for self-assembly involves microsegregation, which is induced by incompatibility between the aromatic rigid core and the alkyl chains, as observed for discotic and polycatenar liquid crystals.[16]

The introduction of heterocyclic moieties into the rigid unit of thermotropic liquid crystals enables their molecular geometry and polarization to be modified, and thus strongly influences their physical properties and mesomorphic behavior.[17] Also, the presence of heteroatoms, such as oxygen, nitrogen, and sulfur atoms, arranged in a non-symmetric distribution, favors the formation of a dipole moment and increases the longitudinal and/or lateral interactions.[18] Moreover, the incorporation of five-membered heteroaromatic rings into the central core of calamitic molecules results in a bent-shaped core, which favors the formation of special kinds of self-assembly. Thus, non linear bent-core liquid crystals based on the oxadiazole heterocycles appear to be of great potential in the search for the nematic biaxial phase.[19]

1,2,4-Oxadiazoles derivatives have already been extensively studied due to their application in medicinal chemistry (anticancer,[20] anti-inflammatory,[21] and anti-HIV agents[22]). However, although this heterocycle also has potential for applications in advanced materials (DLCs or film forming compounds), so far it has not been extensively studied in terms of the properties of such materials.[23]

Thus, this paper presents a new set of bent-rod mesogens (Schemes 1 and 2), which form columnar phases. Besides the synthesis of these molecules derived from 1,2,4-oxadiazole, we report herein a study on the relationship between the chemical structure and the mesomorphic, thermal and optical properties. As far as we know, columnar liquid crystals containing the 1,2,4-oxadiazole unit in their structure have not been previously reported.

* Corresponding author. E-mail address: hugo@qmc.ufsc.br (H. Gallardo).

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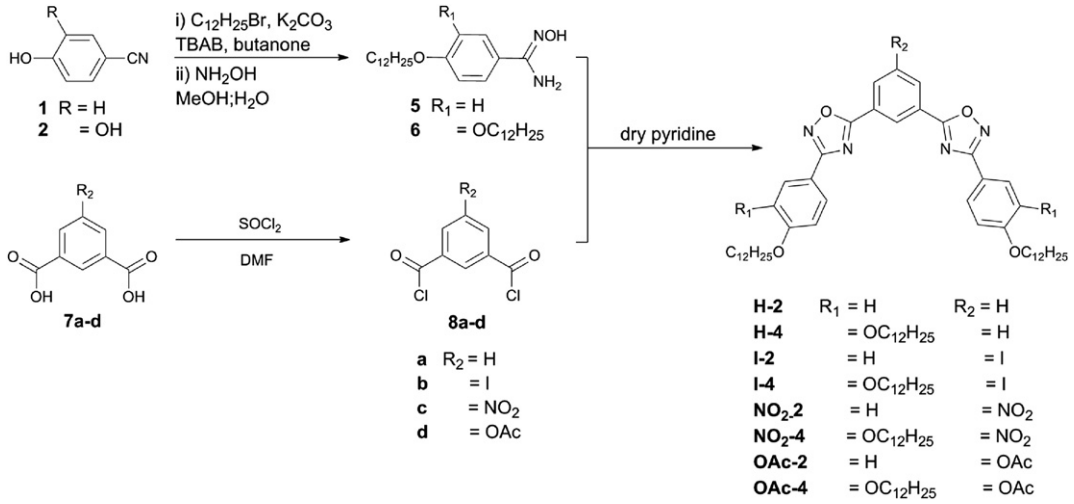
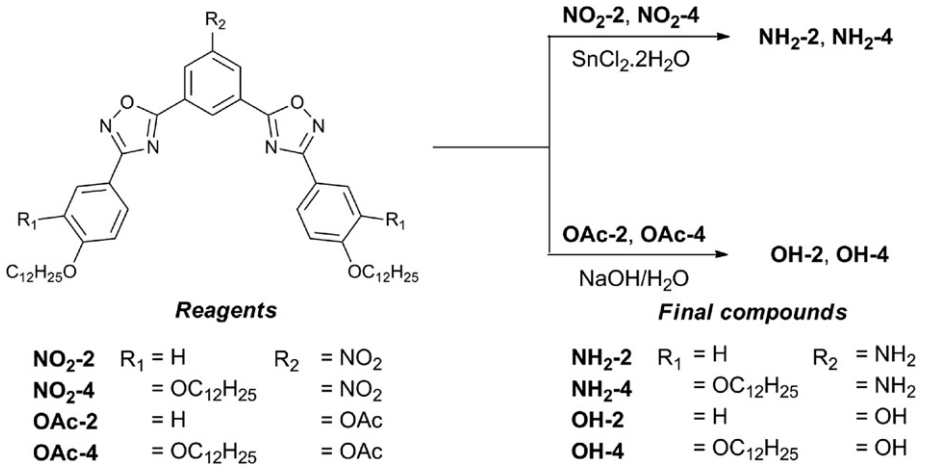



**Scheme 1.** Synthesis of final products (**H-2**, **H-4**, **I-2**, **I-4**, **$NO_2$-2**, and **$NO_2$-4**) and intermediates (**OAc-2** and **OAc-4**). TBAB used only for reaction with compound **2**.




**Scheme 2.** Synthesis of final products (**$NH_2$-2**, **$NH_2$-4**, **OH-2**, and **OH-4**).

## 2. Results and discussion

### 2.1. Synthesis

The synthesis of compounds derived from the 1,2,4-oxadiazole ring was carried out as shown in Scheme 1. Initially, compounds **1** and **2** were alkylated using 1-bromododecane and potassium carbonate (and TBAB for compound **2**), resulting in the intermediate 4-(dodecyloxy)benzonitrile (**3**), and 3,4-bis(dodecyloxy) benzonitrile (**4**), respectively. The intermediates 4-(dodecyloxy)-*N*′-hydroxybenzimidamide (**5**) and 3,4-bis(dodecyloxy)-*N*′-hydroxybenzimidamide (**6**) were then obtained from compounds **3** and **4** by the Tiemann reaction[24] using hydroxylamine hydrochloride and potassium hydroxide in a methanol/water mixture. Finally, the 1,2,4-oxadiazole ring was formed by the reaction between the corresponding amidoximes and the freshly prepared acid dichloride **8a**–**d** in dry pyridine and under reflux, affording the compounds (**H-2**, **H-4**, **I-2**, **I-4**, **$NO_2$-2**, and **$NO_2$-4**) in 34–49% yield.

Compounds **OAc-2** and **OAc-4** were not isolated, since the deprotection was performed in situ with $NaOH_{(aq)}$, resulting in compounds **OH-2** and **OH-4** (Scheme 2) in 62 and 59% yields, respectively. Compounds **$NH_2$-2** and **$NH_2$-4** were prepared from **$NO_2$-2** and **$NO_2$-4** via reduction of the nitro group by $SnCl_2 \cdot 2H_2O$, with 93 and 90% yields, respectively.

The structures of all the compounds were characterized by IR, $^1H$ and $^{13}C$ NMR spectra and elemental analysis.

### 2.2. Thermal and mesomorphic behavior

The mesomorphic properties of the final compounds were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The thermal stability was verified by thermogravimetric analysis (TGA). These results are summarized in Table 1. Four of the ten molecules synthesized showed liquid crystal properties. Compounds **H-4**, **$NH_2$-4**, and **OH-2** showed a monotropic columnar hexagonal ($Col_h$) mesophase, while compound **OH-4** exhibited a very stable enantiotropic $Col_h$ mesophase, with a range of 101.8 °C (Fig. 1). This compound did not show crystallization during cooling (at a rate of 10 °C $min^{-1}$), remaining in a supercooled state until room temperature.

Fig. 2 shows the mesophase characteristic pseudo focal-conic texture, which was observed by POM for compounds **$NH_2$-4** and **OH-2** when the samples were slowly cooled from the isotropic state. This texture, accompanied by large homeotropic domains, is often characteristic of the $Col_h$ mesophase[25] with a preferentially uniaxial character.[26]

A bar graph illustrating the mesophase ranges is shown in the Fig. 3. In general, polycatenar compounds show nematic (N),

**Table 1**
Transition temperatures (°C), enthalpy changes (kJ mol$^{-1}$), and decomposition temperatures (°C) of final compounds

| Compound | Transition[a] | $T$ ($\Delta H$)[a] Heating | $T$ ($-\Delta H$)[a] Cooling | $T_{dec}$[b] |
|---|---|---|---|---|
| **H-2** | Cr-I | 117.9 (37.4) | 107.9 (31.2) | 322 |
| **H-4** | Cr-I | 81.3 (87.2) | | 339 |
| | I-Col$_h$ | | 78.3 (34.6) | |
| | Col$_h$-Cr | | 58.7 (47.2) | |
| **I-2** | Cr-I | 114.0 | 100.7 | 305 |
| **I-4** | Cr-I | 105.7 (61.6) | 89.5 (64.6) | 319 |
| **NO$_2$-2** | Cr-I | 116.8 (68.4) | 100.28 (27.9) | 307 |
| **NO$_2$-4** | Cr-I | 115.0 (49.63) | 99.5 (56.6) | 320 |
| **NH$_2$-2** | Cr-I | 143.0 | 139.0 | 298 |
| **NH$_2$-4** | Cr-I | 131.1 (24.2) | | 321 |
| | I-Col$_h$ | | 130.8 (16.5) | |
| | Col$_h$-Cr | | 98.7 (13.9) | |
| **OH-2** | Cr-I | 121.5 (24.9) | | 300 |
| | I-Col$_h$ | | 107.4 (25.0) | |
| | Col$_h$-Cr | | 61.8 (13.7) | |
| **OH-4** | Cr-Col$_h$ | 82.8 (56.3) | 176.9 (5.6) | 309 |
| | Col$_h$-I | 184.6 (7.4) | | |

Cr=crystal phase; Col$_h$=hexagonal columnar phase; I=isotropic liquid.
[a] Transition determined by DSC and POM at a scan rate of 10 °C min$^{-1}$.
[b] Thermogravimetric measurements referring to the beginning of decomposition under a nitrogen atmosphere with heating rate of 10 °C min$^{-1}$.

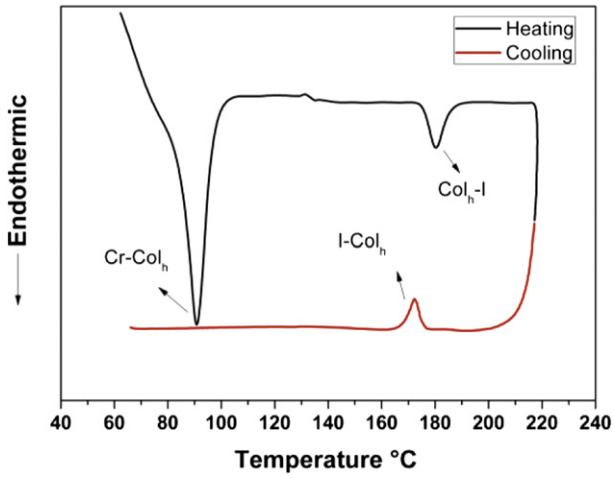



**Fig. 1.** Thermogram obtained by DSC analysis of second heating and cooling at 10 °C min$^{-1}$ showing the thermal transitions for compound **OH-4**.

smectic (Sm), columnar (Col), and/or cubic mesophases, depending on their molecular structure and also on the number and position of the terminal alkyl chains, the core length and polar substituents.[27] Some final compounds have the thermal properties of an ordinary solid. This difference in the mesomorphic behavior in

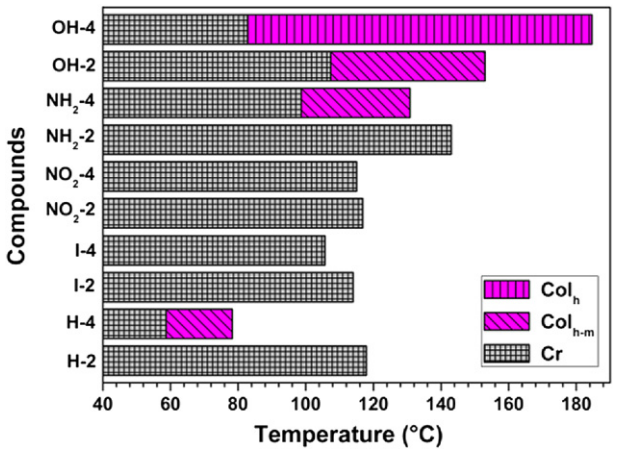



**Fig. 3.** Bar graph showing the phase behavior of the final compounds. Col$_h$=enantiotropic liquid crystal; Col$_{h-m}$=monotropic liquid crystal.

comparison with **H-4**, **NH$_2$-4**, **OH-2**, and **OH-4** can be explained by the tendency for hydrogen-bonding, dipole, and steric interactions to occur.[16b] In the case of the compounds **NH$_2$-4**, **OH-2**, and **OH-4**, the formation of hydrogen-bonds prevents the free rotation of the substituent groups, this being responsible for the unique packing.

The TGA investigation of these new bent-rod mesogens derived from 1,2,4-oxadiazole indicated that they have good thermal stability, with decomposition temperatures ranging between 298 and 339 °C. Also, we noted that the compounds containing four aliphatic chains (**H-4**, **I-4**, **NO$_2$-4**, **NH$_2$-4**, and **OH-4**) are slightly more stable than the compounds with only two (**H-2**, **I-2**, **NO$_2$-2**, **NH$_2$-2**, and **OH-2**). Furthermore, both products without substituent (**H-2** and **H-4**) are more stable than the other molecules. Compounds with four aliphatic chains showed lower melting points than compounds with two aliphatic chains.

### 2.3. X-ray diffraction studies

The mesophase assignments made by POM were ratified by X-ray diffraction analysis. The diffractogram patterns obtained are characteristic of a hexagonal columnar arrangement, where the reflection peaks in the low-angle region were attributed as (10), (11), (20), and (21) with a reciprocal spacing ratio of 1:$\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$.[8a,28] The observed values ($d$, obsd) were determined by applying the Bragg's Law to the diffracted angles $\theta$ and are summarized in Table 2. The calculated values ($d$, calcd) where obtained by assuming the first maximum (10) and then the second order peaks were calculated assuming a hexagonal structure, in order to compare with the measured values and to confirm the hexagonal

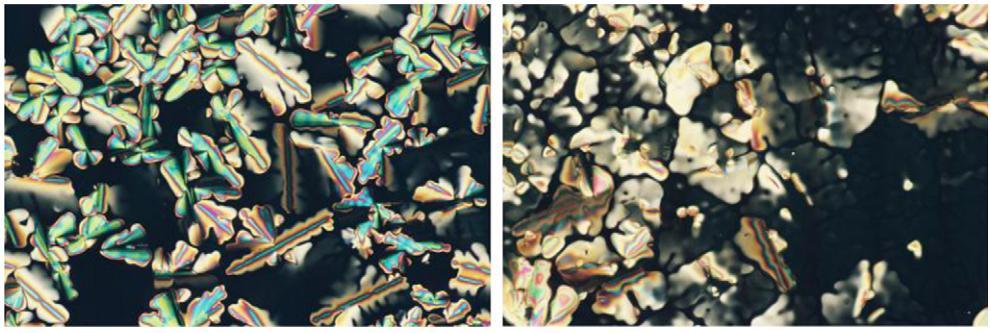


**Fig. 2.** Polarized optical micrographs of columnar phases formed upon cooling from isotropic phase (200×): observed for compound **NH$_2$-4** at 130.3 °C (left) and compound **OH-2** at 107.0 °C (right).

**Table 2**
X-ray diffraction data for final compounds in mesophases

| Compound | Mesophase | Miller indices | *d*, obsd (Å) | *d*, calcd (Å) | *a* (Å) | *L*[a] (Å) |
|---|---|---|---|---|---|---|
| **H-4** | $Col_h$ at 75 °C | 10 | 34.6 | 34.6 | 40.0 | 28.6 |
| | | 11 | 20.1 | 20.0 | | |
| | | 20 | 17.2 | 17.3 | | |
| | | 21 | 13.1 | 13.1 | | |
| | | | 7.0 (br) | | | |
| | | | 4.6 (br) | | | |
| | | | 3.5 (br) | | | |
| **$NH_2$-4** | $Col_h$ at 130 °C | 10 | 36.9 | 36.9 | 42.6 | 30.0 |
| | | 20 | 18.5 | 18.5 | | |
| | | | 7.0 (br) | | | |
| | | | 4.6 (br) | | | |
| | | | 3.5 (br) | | | |
| **OH-2** | $Col_h$ at 105 °C | 10 | 36.9 | 36.9 | 42.6 | 31.0 |
| | | 20 | 19.3 | 18.5 | | |
| | | | 4.6 (br) | | | |
| | | | 3.5 (br) | | | |
| **OH-4** | $Col_h$ at 180 °C | 10 | 33.5 | 33.5 | 38.7 | 28.0 |
| | | 11 | 19.5 | 19.3 | | |
| | | 20 | 16.7 | 16.8 | | |
| | | | 7.1 (br) | | | |
| | | | 4.6 (br) | | | |
| | | | 3.5 (br) | | | |

[a] *L* estimated by ChemBio3D Ultra Software, version 11.0.1.

phase. The lattice constant (*a*) was obtained by following reports in the literature.[29] The rigid core length (*L*) of the proposed structures (dimer, trimer, and tetramer) inside a single disc was calculated in order to make comparisons with the lattice constant.

Fig. 4 shows the X-ray diffraction pattern of compound **OH-4** in the columnar phase at 180 °C, where the position of the peaks and the respective distances are indicated. All the liquid crystalline compounds exhibited similar diffractograms with a broad reflection at around 3.5 Å, which is consistent with the π–π stacking between neighboring mesogens within individual columns. This may indicate a highly ordered mesophase, i.e., a long-range order along the columns. In addition, the characteristic diffuse peak at around 4.6 Å corresponds to the liquid-like order between the alkyl chains. The broad peak at around 7.0 Å is consistent with the repetition of the distance of two alternated ordered discs. By comparing the rigid core length, *L*, with the distance between the center of two columns in the hexagonal structure, given by *a*, one can see that the difference varies from 10.7 Å–12.6 Å. The maximum value estimated for one side chain is 16.0 Å, indicating that all the compounds may present interdigitation of the alkoxy chains or non linear conformations.[30]

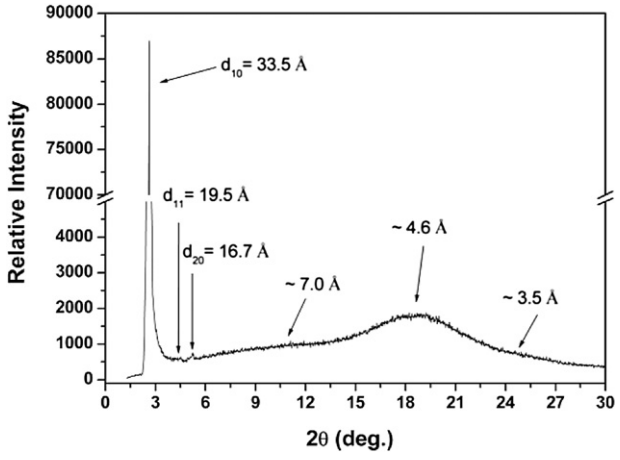



**Fig. 4.** X-ray diffraction pattern of the hexagonal columnar mesophase of **OH-4** at 180 °C.

Based on the results obtained from the X-ray experiments and considering the density of these materials as 1 g $cm^{-3}$, the number of molecules per average unit cell (*Z*) can be obtained according to reports in the literature.[31] The *Z* value for **H-4** and **$NH_2$-4** is three, which leads to the formation of discs with a total of twelve alkoxy chains. The mesomorphism observed for **H-4** is the result of a microsegregation between the aliphatic parts and the polar parts inside the disc.[32] However, for **$NH_2$-4** the molecules arranged within the disc can form hydrogen-bonds between the amine groups. There are four molecules for the **OH-2** unit disc, resulting in a total of eight alkoxy chains. These molecules are arranged within the disc probably with hydrogen-bonding between the hydroxyl groups. In the case of **H-4** or compounds **$NH_2$-4** and **OH-2**, the absence of additional stabilization forces leads to the formation of monotropic $Col_h$ mesophases. On the other hand, for the compound **OH-4**, there are two molecules per unit disc resulting in eight alkoxy chains.

This compound showed an enantiotropic $Col_h$ phase with a very stable mesomorphism, which can be attributed to the formation of a dimer through hydrogen-bonding between the hydroxyl group and the oxadiazole ring nitrogen[33] (see Fig. 5).

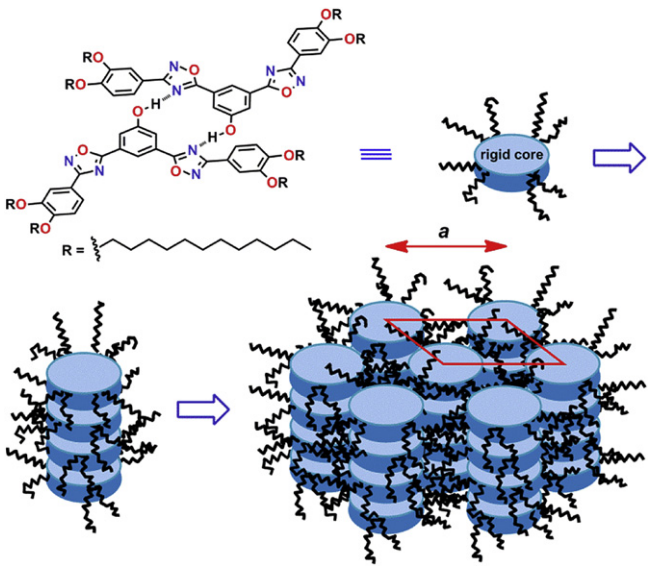



**Fig. 5.** Suggested molecular organization inside the hexagonal columnar phase based on X-ray data obtained for **OH-4**.

For comparison purposes, we prepared the same compound **OH-4** but with a chain length of only 6 carbons, **OH-4 $C_6$**. This new compound also shows columnar mesomorphism (Cr 144.2 $Col_h$ 176.5 I °C). These results corroborates with our evidences of columnar arrangement promoted by hydrogen-bonding, once that there is no formation of smectic phases, which would indicate a polycatenar behavior (for DSC, mesophase texture and XRD analysis, see Supplementary data).

IR spectroscopy was used to examine the hydrogen-bonding in this dimer. The IR spectra were run on a Varian 3100 FT-IR spectrometer. Fig. 6 shows the infrared spectra in solid state (KBr) at room temperature and for a sample that was heated to a temperature of 195 °C and then cooled slowly to room temperature, the two samples were examined between 4000 and 450 $cm^{-1}$. The formation of hydrogen-bonds in the dimer is detected through the modification of the O–H stretching vibrations. The ν-OH band in the solid state at ca. 3290 $cm^{-1}$ is shifted by ca. 40 $cm^{-1}$ in the liquid crystal phase (new band centered at ≈3250 $cm^{-1}$). This is indicative of the formation of a stronger hydrogen bond in the dimer.

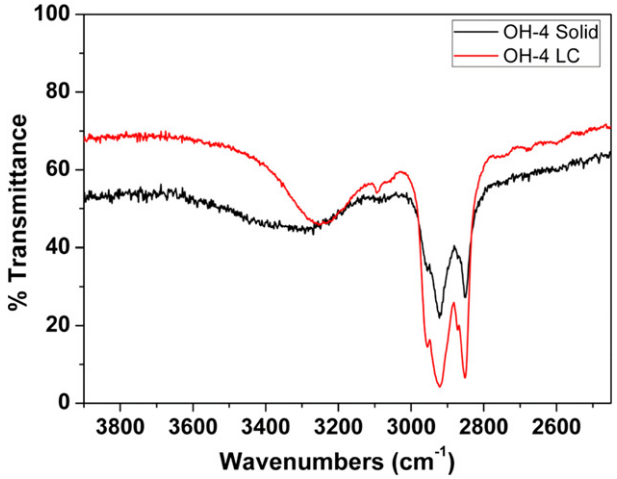



**Fig. 6.** The infrared spectra in solid state and liquid crystals (KBr) at room temperature for **OH-4**.

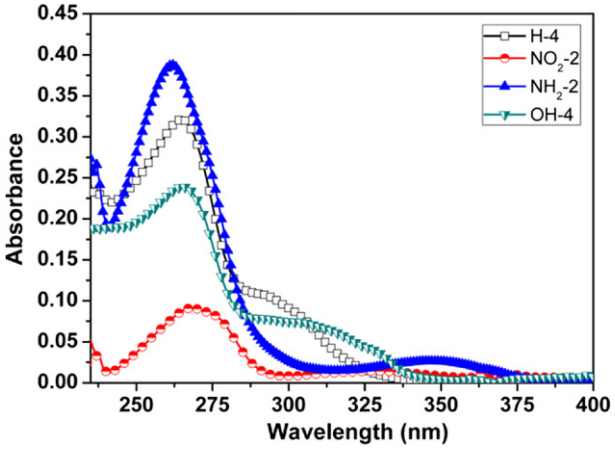



**Fig. 7.** Optical absorption spectra of the final compounds **H-4**, **$NO_2$-2**, **$NH_2$-2**, and **OH-4**, in chloroform solution.

The microsegregation between the aliphatic parts and the polar parts inside a single disc may explain the absence of mesomorphism in the compound analogue containing I and $NO_2$ groups, as efficient packing of molecules is sterically disfavored by the incorporation of volumous I and $NO_2$. The *Z* number observed in all mesomorphic cases is consistent with the number of alkoxy chains usually required for columnar phases to be present. Liquid crystal behavior was found for systems with eight and twelve alkoxy chains.[34]

## 2.4. Absorption properties

The UV–vis spectroscopy data for the 1,2,4-oxadiazole final compounds in chloroform and in thin film are summarized in Table 3.

All compounds exhibited similar absorptions between 250 and 270 nm, having maxima between 262 and 267 nm. In Fig. 7 four representative examples are shown. These absorption bands are attributed to the $\pi-\pi^*$ transitions in the heteroaromatic portion of the molecule due to the high molar absorption coefficient ($\varepsilon$=1.8–8.1×$10^4$ L $mol^{-1}$ $cm^{-1}$). For compounds **H-4**, **I-4**, **$NO_2$-4**, **$NH_2$-4**, and **OH-4** a shoulder and for **$NH_2$-2** and **OH-2** a minor energy band is observed between 292 and 347 nm. This second band corresponds to an $n-\pi^*$ transition. Absorption spectra were also carried out in different solvents as benzene, methanol, and acetonitrile, and the same pattern were observed. Stokes shift were calculated considering de minor absorption energy band and emission maxima band.[35] These compounds exhibited blue emission in solution ($\lambda_{abs}^{max}$=331–457 nm) with stokes shifts between 38 and 156 nm.

Compounds **$NO_2$-2** and **$NO_2$-4** showed weakly fluorescence emission band, therefore, Stokes shift was not calculated.

The optical absorption and emission of the final compounds in the solid state were measured in thin films, obtained by spin-coating from chloroform solution onto a quartz plate. The compounds also showed fluorescence in the solid phase (with the exception of compounds **$NO_2$-2**, **$NO_2$-4**), exhibiting emission maxima at wavelengths between 388 and 506 nm. Most of the compounds showed a red-shift in the solid state spectrum compared with their emission wavelengths in chloroform solution while compounds **H-2**, **H-4**, and **I-4** showed blue-shifts.

## 3. Conclusions

A new series derived from heterocyclic 1,2,4-oxadiazole was prepared and characterized. The mesomorphic and photophysical behavior were studied. Four compounds presented liquid–crystalline phases, characterized by POM and DSC. The nature of the mesophases was established by XRD studies. These materials showed a tendency toward hexagonal columnar mesomorphism. Their ability to form $Col_h$ despite their bent-rod shape may be explained by dipole, steric interactions, and hydrogen-bonding producing a dimer, trimer, and tetramer inside a single disc, allowing the formation of a columnar phase, which was observed in

**Table 3**
Summary of photophysical properties of the final compounds

| Compound | $\lambda_{abs}^{max}$/nm[a] ($\varepsilon$/$10^4$)[b] | $\lambda_{em}^{max}$/nm[a,c] | Stokes shift/nm[a] | $\lambda_{abs}^{max}$/nm[d] | $\lambda_{em}^{max}$/nm[d,c] | Stokes shift/nm[d] |
|---|---|---|---|---|---|---|
| **H-2** | 262 (2.3) | 398 | 136 | 252 | 388 | 136 |
| **H-4** | 265 (6.4)/303 (2.1) | 440 | 137 | 246; 311 | 407 | 96 |
| **I-2** | 264 (6.2) | 331 | 67 | 259; 367 | 506 | 139 |
| **I-4** | 267 (6.4)/301 (2.3) | 457 | 156 | 260 | 424 | 164 |
| **$NO_2$-2** | 268 (1.8)/328 (0.3) | —[e] | —[e] | 263 | —[e] | —[e] |
| **$NO_2$-4** | 266 (2.1)/293 (1.0) | —[e] | —[e] | 263; 300 | —[e] | —[e] |
| **$NH_2$-2** | 262 (7.8)/347 (0.5) | 395 | 48 | 300; 369 | 497 | 128 |
| **$NH_2$-4** | 263 (7.4)/292 (2.5)/344 (0.7) | 396 | 52 | 262; 362 | 430 | 68 |
| **OH-2** | 263 (8.1)/317 (0.8) | 355 | 38 | 259; 338 | 423 | 85 |
| **OH-4** | 265 (4.8)/307 (1.4) | 448 | 141 | 263; 325 | 446 | 121 |

[a] Measured in $CHCl_3$ (5.0×$10^{-6}$ mol $L^{-1}$).
[b] Units=L $mol^{-1}$ $cm^{-1}$.
[c] Excited at absorption maxima in low energy band.
[d] Data recorded from solid thin films.
[e] **$NO_2$-2** and **$NO_2$-4** are not fluorescents in chloroform solution and solid state.

the X-ray diffraction studies. The compound **OH-4** displays a stable liquid crystal phase over a broad temperature range including at room temperature after annealing. All of the compounds had good thermal stability with decomposition temperatures higher than 298 °C. The photophysical properties of these compounds, in solution and in solid state, were evaluated, showing weak blue emission in solution and variable Stokes shifts of between 38 and 156 nm.

## 4. Experimental

### 4.1. Materials and characterizations

The chemicals used in this study were 1-bromododecane (98%, Acros Organics), 4-hydroxyacetanilide (98%, Sigma–Aldrich), 3,4-dihydroxybenzonitrile (97%, Sigma–Aldrich), isophthalic acid (**7a**) (99%, Sigma–Aldrich), 5-nitroisophthalic acid (**7c**) (98%, Acros Organics), 5-aminoisophthalic acid (98+%, Acros Organics), 5-hydroxyisophthalic acid (99%, Acros Organics). All other inorganic and organic reagents and solvents were purchased from commercial sources (Sigma–Aldrich, Merck, Acros, Vetec, and Synth) and used as received. Pyridine was dried by distillation over KOH, and used as specified. Purifications by column chromatography used on silica gel 60–200 mesh 60 Å (Acros), and recrystallization from commercial grade solvents. Infrared spectra were recorded on a Perkin–Elmer model 283 spectrometer using KBr discs. $^1$H and $^{13}$C NMR were recorded using a Varian Mercury Plus spectrometer operating at 400 and 100.6 MHz, respectively, using TMS as the internal standard. Elemental analysis was carried out using a Carlo Erba model E-1110 instrument. The compounds 5-iodoisophthalic acid (**7b**)[36] and 5-acetoxyisophthalic acid (**7d**)[37] were prepared by literature methods.

### 4.2. Thermal analysis

The melting points, thermal transition and mesomorphic textures were observed with an Olympus BX50 microscope, equipped with a Mettler Toledo FP 82 hot stage and a PM-30 exposure control unit. DSC measurements were carried out using a Shimadzu instrument with a DSC-50 module. Thermal transitions were determined at a scan rate of 10 °C min$^{-1}$ and a nitrogen flow of 50 mL min$^{-1}$. The thermal stability was analyzed using Shimadzu equipment with a TGA-50 module at a heating rate of 10 °C min$^{-1}$ and nitrogen flow of 50 mL min$^{-1}$.

### 4.3. X-ray diffraction analysis

The X-ray diffraction experiments were carried out with the X'PERT-PRO (PANalytical) diffractometer using Cu Kα radiation ($\lambda$=1.5418 Å), with an applied power of 1.2 kVA. The scans were performed in continuous mode from 2° to 30° (2$\theta$ angle) and the diffracted radiation collected with an the X'Celerator detector. The samples were prepared by prior heating (with a hot stage) of an amount of powder on a glass plate until the compound melted to the liquid state, followed by cooling to room temperature. As a result, we obtain a film approximately 1 mm thick. The films were then placed in the diffractometer chamber on the TCU2000 temperature control unit (Anton Paar), which allows control of the sample temperature during the measurement. The films were first heated until the isotropic phase and the diffraction patterns collected during cooling back through the mesophases.

### 4.4. UV–vis absorption and fluorescence spectroscopy

An HP UV–vis model 8453 spectrophotometer was used to record absorption spectra in solution, while the fluorescence spectra were recorded on a Hitachi-F-4500. For the measurements in solid state (thin films) an OceanOptics USB4000 spectrophotometer was used.

We produced thin films of the compounds on glass plates using the spin-coating technique for the absorption and fluorescence measurements in solid state. The glass plates were first carefully cleaned by washing with neutral detergent followed by a sequence of 30-min sonications in acetone, alcohol, and water, and finally dried in an oven. The solutions were prepared with chloroform at a concentration of 2% (wt) and the films produced after spinning at 2000 rpm for 30 s, at room temperature.

### 4.5. Synthesis

*4.5.1. 4-(Dodecyloxy)benzonitrile (**3**).* Firstly, 15.00 g (126.0 mmol) of 4-hydroxybenzonitrile (**1**), 42.30 mL (176.0 mmol) of 1-bromododecane, 52.20 g (378.0 mmol) of $K_2CO_3$, and 350 mL of butanone were placed into a 500 mL round-bottomed flask equipped with a condenser. The mixture was then refluxed and stirred for 24 h. After this period, the suspension was filtered and washed with hot butanone. The solvent was removed by rotary evaporation and the solid obtained was recrystallized on ethanol, affording 33.60 g of a white crystals (93%), mp 41.5–44.0 °C (lit. 42–43 °C).[25] IR (KBr, cm$^{-1}$): $\nu_{max}$: 2916, 2850, 2218 (C≡N), 1608, 1509, 1302, 1256, 1172, 833, 547. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 7.55 (d, $J$=8.9 Hz, 2H, Ar–H), 6.92 (d, $J$=8.9 Hz, 2H, Ar–H), 3.98 (t, $J$=6.6 Hz, 2H, $-OCH_2-$), 1.78 (qt, $J$=6.6 Hz, 2H, $-OCH_2CH_2-$), 1.44 (m, 2H, $-CH_2-$), 1.22–1.33 (br, 16H, $-CH_2-$), 0.87 (t, $J$=6.7 Hz, 3H, $-CH_3$). $^{13}$C NMR ($CDCl_3$), $\delta$, ppm: 162.7, 134.2, 119.5, 115.4, 103.8, 68.6, 32.2, 29.9, 29.9, 14.9.

*4.5.2. 3,4-Bis(dodecyloxy)benzonitrile (**4**).* Firstly, 12.00 g (88.9 mmol) of 3,4-dihydroxybenzonitrile (2), 53.40 mL (222.2 mmol) of 1-bromododecane, 49.07 g (355.6 mmol) of $K_2CO_3$, 1.43 g (4.44 mmol) of TBAB, and 350 mL of butanone were placed into a 500 mL round-bottomed flask equipped with a condenser. The mixture was then refluxed and stirred for 24 h. After this period the suspension was filtered, washed with hot butanone and the solvent was removed by rotary evaporation. The solid obtained was recrystallized over acetonitrile, yielding 39.80 g of a white solid (95%), mp 82.0–82.5 °C (lit. 81–83 °C).[25] IR (KBr, cm$^{-1}$): $\nu_{max}$: 2954, 2918, 2872, 2849, 2221 (C≡N), 1597, 1581, 1519, 1468, 1422, 1280, 1244, 1139, 992, 85, 812, 722. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 7.23 (dd, $J$=8.4 Hz and 1.9 Hz, 1H, Ar–H); 7.07 (d, $J$=1.9 Hz, 1H, Ar–H); 6.86 (d, $J$=8.4 Hz, 1H, Ar–H); 4.02 (t, $J$=6.6 Hz, 2H, $-OCH_2-$); 3.98 (t, $J$=6.6 Hz, 2H, $-OCH_2-$); 1.83 (m, 4H, $-OCH_2CH_2-$); 1.46 (m, 4H, $-CH_2-$); 1.25–1.36 (br, 32H, $-CH_2-$); 0.88 (t, $J$=6.7 Hz, 6H, $-CH_3$). $^{13}$C NMR (DMSO-$d_6$, −90 °C), $\delta$, ppm: 151.8, 147.7, 125.1, 117.6, 115.8, 112.9, 108.0, 68.1, 67.6, 29.9, 27.6, 27.6, 27.5, 27.3, 27.2, 24.1, 20.6, 12.3.

### 4.6. Synthesis of amidoximes (5,6)

General procedure. Firstly, 41.8 mmol of the appropriate nitrile 3 or 4 and 200 mL of methanol were placed into a 500 mL round-bottomed flask equipped with a condenser and 92.0 mmol of $NH_2OH{\cdot}HCl$ and 92.0 mmol of KOH dissolved in 200 mL of methanol/water 8:2 were then added. The resultant mixture was kept under reflux for 24 h. After this period the solvent was removed by rotary evaporation and the solid was washed with plenty of water. The solid obtained was recrystallized on ethanol.

*4.6.1. 4-(Dodecyloxy)-N′-hydroxybenzimidamide (**5**).* Yield: 85% of a white solid, mp 81–83 °C (lit. 81–82 °C).[38] IR (KBr, cm$^{-1}$): $\nu_{max}$: 3450, 3350, 2920, 2853, 1654, 1611, 1521, 1394, 1253, 826. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 7.55 (d, $J$=8.9 Hz, 2H, Ar–H), 6.90 (d, $J$=8.9 Hz, 2H, Ar–H), 4.82 (br, 2H, $-NH_2$), 3.97 (t, $J$=6.6 Hz, 2H, $-OCH_2-$), 1.78 (qt,

$J$=6.6 Hz, 2H, $-OCH_2CH_2-$), 1.46 (m, 2H, $-CH_2-$), 1.38–1.22 (m, 16H, $-CH_2-$), 0.88 (t, $J$=6.6 Hz, 3H, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 160.6, 152.6, 127.1, 124.6, 114.5, 68.1, 31.9, 29.6, 29.6, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1.

*4.6.2. 3,4-Bis(dodecyloxy)-N′-hydroxybenzimidamide (**6**).* Yield: 93% of white solid, mp 88.5–88.9 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3449, 3351, 3182, 2919, 2849, 1640, 1592, 1518, 1469, 1440, 1388, 1332, 1265, 1228, 1143, 1125, 724. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 7.18 (s, 1H, Ar–H), 7.12 (d, $J$=8.3 Hz, 1H, Ar–H), 6.86 (d, $J$=8.3 Hz, 1H, Ar–H), 4.83 (br, 2H, $-NH_2$), 4.01 (m, 4H, $-OCH_2-$), 1.81 (m, 4H, $-OCH_2CH_2-$), 1.46 (m, 4H, $-CH_2-$), 1.30–1.24 (m, 32H, $-CH_2-$), 0.88 (t, $J$=6.6 Hz, 6H, $-CH_3$). $^{13}C$ NMR (MHz, $CDCl_3$), $\delta$, ppm: 153.1, 150.9, 149.3, 125.3, 118.6, 113.3, 111.5, 69.5, 68.4, 32.2, 30.0, 29.9, 29.9, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.9, 14.4.

### 4.7. Synthesis of 1,2,4-oxadiazoles

General procedure. Firstly, 0.5 g of the corresponding acid **7a**–**d**, 3 mL of $SOCl_2$ and 1 drop of DMF were placed inside a round-bottomed flask equipped with a condenser and a drying tube. The mixture was then refluxed for 4 h. The excess $SOCl_2$ was removed by vacuum distillation and 2.4 equiv of the hydroxylamine (5, 6) and 9 mL of dry pyridine were added to the mixture, which was refluxed for a further 24 h. After this period the solution was cooled to room temperature and poured into 200 mL of ice/water. The precipitate was filtered, washed with plenty of water, and purified.

*4.7.1. 1,3-Bis(3-(4-(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl)benzene (**H-2**).* The crude product was purified by column chromatography (silica gel, $CH_2Cl_2$), to give white solid, yield 35%, mp 117.9 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3070, 2923, 2852, 1610, 1548, 1469, 1421, 1362, 1253, 1172, 758. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 9.05 (t, 1H, $J$=1.8 Hz, Ar–H), 8.42 (dd, 2H, $J$=7.8 Hz and $J$=1.8 Hz, Ar–H), 8.13 (d, 4H, $J$=8.4 Hz, Ar–H), 7.75 (t, 1H, $J$=7.8 Hz, Ar–H), 7.02 (d, 4H, $J$=8.4 Hz, Ar–H), 4.04 (t, 4H, $J$=6.4 Hz, $-OCH_2-$), 1.82 (qt, 4H, $J$=6.4 Hz, $-OCH_2CH_2-$), 1.47 (m, 4H, $-CH_2-$), 1.41–1.22 (m, 32H, $-CH_2-$), 0.88 (t, 6H, $J$=6.4 Hz, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 174.2, 168.9, 161.7, 131.7, 130.0, 129.2, 127.7, 125.5, 118.8, 114.8, 68.2, 31.9, 29.7, 29.64, 29.60, 29.6, 29.4, 29.4, 29.2, 29.0, 22.7, 14.1. Elemental analysis $C_{46}H_{62}N_4O4$: required C, 75.17; H, 8.50; N, 7.62; Found: C, 74.94; H, 8.95; N, 7.83%.

*4.7.2. 1,3-Bis(3-(3,4-bis(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl) benzene (**H-4**).* The solid obtained was purified by column chromatography (silica gel, $CH_2Cl_2$), followed by recrystallization on ethyl acetate, yielding 34% of a white solid, mp 81.3 °C (monotropic liquid crystal) I, −78.3 °C—$Col_h$, −58.7 °C—Cr. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3069, 2919, 2850, 1607, 1555, 1501, 1467, 1263, 1223, 751. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 9.06 (s, 1H, Ar–H), 8.44 (d, 2H, $J$=7.8 Hz, Ar–H), 7.78 (d, 2H, $J$=8.2 Hz, Ar–H), 7.75 (t, 1H, $J$=7.8 Hz, Ar–H), 7.69 (s, 2H, Ar–H), 6.99 (d, 2H, $J$=8.2 Hz, Ar–H), 4.13 (t, 4H, $J$=6.4 Hz, $-OCH_2-$), 4.08 (t, 4H, $J$=6.6 Hz, $-OCH_2-$), 1.88 (qt, 4H, $J$=6.6 Hz, $-OCH_2CH_2-$), 1.86 (qt, 4H, $J$=6.4 Hz, $-OCH_2CH_2-$), 1.52 (qt, 4H, $J$=6.4 Hz, $-CH_2-$), 1.50 (qt, 4H, $J$=6.6 Hz, $-CH_2-$), 1.42–1.24 (br, 64H, $-CH_2-$), 0.88 (t, 12H, $J$=6.4 Hz, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 174.4, 169.3, 152.1, 149.5, 132.0, 130.2, 128.0, 125.8, 121.3, 119.2, 113.2, 112.4, 69.6, 69.3, 32.2, 29.9, 29.7, 29.6, 29.5, 29.4, 26.3, 26.3, 22.9, 14.4. Elemental analysis $C_{70}H_{110}N_4O_6$: required C, 76.18; H, 10.05; N, 5.08; Found: C, 75.46; H, 10.55; N, 5.00%.

*4.7.3. 5,5′-(5-Iodo-1,3-phenylene)bis(3-(4-(dodecyloxy)phenyl)-1,2,4-oxadiazole) (**I-2**).* The product was recrystallized once over 2-propanol and once over acetonitrile, obtaining 42% of a white solid, mp 114.0 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 2914, 2848, 1626, 1540, 1471, 1416, 1350, 1242, 1172, 834, 756. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 8.98 (t, 1H, $J$=1.6 Hz, Ar–H), 8.75 (d, 2H, $J$=1.6 Hz, Ar–H), 8.11 (d, 4H, $J$=8.7 Hz, Ar–H), 7.02 (d, 4H, $J$=8.7 Hz, Ar–H), 4.04 (t, 4H, $J$=6.6 Hz, $-OCH_2-$), 1.82 (qt, 4H, $J$=6.6 Hz, $-OCH_2CH_2-$), 1.48 (m, 4H, $-CH_2-$), 1.41–1.25 (br, 32H, $-CH_2-$), 0.88 (t, 6H, $J$=6.6 Hz, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 173.0, 169.2, 162.0, 140.4, 129.4, 127.2, 126.8, 118.8, 115.1, 94.8, 68.4, 32.2, 29.8, 29.6, 29.6, 29.4, 26.3, 22.9, 14.4. Elemental analysis $C_{46}H_{61}IN_4O_4$: required C, 64.18; H, 7.14; N, 6.51; Found: C, 64.05; H, 7.40; N, 6.42%.

*4.7.4. 5,5′-(5-Iodo-1,3-phenylene)bis(3-(3,4-bis(dodecyloxy)phenyl)-1,2,4-oxadiazole) (**I-4**).* The product was recrystallized twice from 2-propanol, to afford 40% of a light violet solid, mp 105.7 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 2951, 2851, 1605, 1551, 1497, 1486, 1470, 1448, 1388, 1339, 1221, 1226, 1139, 1122, 756. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 8.98 (t, 1H, $J$=1.5 Hz, Ar–H); 8.76 (d, 2H, $J$=1.5 Hz, Ar–H); 7.76 (dd, 2H, $J$=8.6 Hz and $J$=1.8 Hz, Ar–H); 7.66 (d, 2H, $J$=1.8 Hz, Ar–H); 6.98 (d, 2H, $J$=8.6 Hz, Ar–H); 4.13 (t, 4H, $J$=6.4 Hz, $-OCH_2-$); 4.08 (t, 4H, $J$=6.6 Hz, $-OCH_2-$); 1.88 (qt, 4H, $J$=6.6 Hz, $-OCH_2CH_2-$); 1.86 (qt, 4H, $J$=6.4 Hz, $-OCH_2CH_2-$), 1.52 (qt, 4H, $J$=6.4 Hz, $-CH_2-$), 1.50 (qt, 4H, $J$=6.6 Hz, $-CH_2-$), 1.42–1.22 (br, 64H, $-CH_2-$), 0.88 (dt, 12H, $J$=6.6 Hz, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 172.7, 169.1, 151.9, 149.2, 140.1, 126.9, 126.6, 121.0, 118.6, 112.9, 112.0, 94.6, 69.3, 69.1, 31.9, 29.6, 29.6 29.4, 29.4, 29.2, 29.1, 26.0, 26.0, 22.7, 14.1. Elemental analysis $C_{70}H_{109}IN_4O6$: required C, 68.38; H, 8.94; N, 4.56; Found: C, 68.05; H, 9.08; N, 4.59%.

*4.7.5. 5,5′-(5-Nitro-1,3-phenylene)bis(3-(4-(dodecyloxy)phenyl)-1,2,4-oxadiazole) (**NO$_2$-2**).* The solid obtained was purified by column chromatography (silica gel, $CH_2Cl_2$), followed by recrystallization on ethyl acetate. Light yellow solid, yield 49%, mp 116.8 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 2924, 2851, 1611, 1540, 1348, 1254, 1172. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 9.31 (t, 1H, $J$=1.6 Hz, Ar–H), 9.24 (d, 2H, $J$=1.6 Hz, Ar–H), 8.14 (d, 4H, $J$=8.8 Hz, Ar–H), 7.04 (d, 4H, $J$=8.8 Hz, Ar–H), 4.05 (t, 4H, $J$=6.6 Hz, $-OCH_2-$), 1.83 (qt, 4H, $J$=6.6 Hz, $-OCH_2CH_2-$), 1.49 (m, 4H, $-CH_2-$), 1.41–1.22 (br, 32H, $-CH_2-$), 0.88 (t, 6H, $J$=6.6 Hz, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 172.4, 169.5, 162.2, 149.4, 132.5, 129.5, 127.5, 126.2, 118.4, 115.1, 68.5, 32.2, 29.9, 29.9, 29.8, 29.8, 29.6, 29.59, 29.4, 26.2, 22.9, 14.4. Elemental analysis $C_{46}H_{61}N_5O_6$: required C, 70.83; H, 7.88; N, 8.98; Found: C, 70.84; H, 8.00; N, 8.93.

*4.7.6. 5,5′-(5-Nitro-1,3-phenylene)bis(3-(3,4-bis(dodecyloxy)phenyl)-1,2,4-oxadiazole) (**NO$_2$-4**).* The crude product was purified by column chromatography (silica gel, $CH_2Cl_2$) and recrystallized over ethyl acetate. The yield was 34% of a light yellow powder, mp 115.0 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3069, 2919, 2850, 1608, 1537, 1467, 1349, 1280, 1227, 742. $^1H$ NMR ($CDCl_3$), $\delta$, ppm: 9.31 (s, 1H, Ar–H), 9.25 (s, 2H, Ar–H), 7.79 (d, 2H, $J$=8.3 Hz, Ar–H), 7.67 (s, 2H, Ar–H), 6.99 (d, 2H, $J$=8.3 Hz, Ar–H), 4.13 (t, 4H, $J$=6.7 Hz, $-OCH_2-$), 4.08 (t, 4H, $J$=6.6 Hz, $-OCH_2-$), 1.89 (qt, 4H, $J$=6.6 Hz, $-OCH_2CH_2-$), 1.87 (qt, 4H, $J$=6.7 Hz, $-OCH_2CH_2-$), 1.51 (m, 8H, $-CH_2-$), 1.44–1.21 (br, 64H, $-CH_2-$), 0.88 (m, 12H, $-CH_3$). $^{13}C$ NMR ($CDCl_3$), $\delta$, ppm: 172.4, 169.6, 152.4, 149.6, 149.4, 132.5, 127.5, 126.2, 121.4, 118.5, 113.2, 112.3, 69.6, 69.36, 32.2, 29.9, 29.9, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.9, 14.4. Elemental analysis $C_{70}H_{109}N_5O_8$: required C, 73.19; H, 9.56; N, 6.10; Found: C, 72.78; H, 10.55; N, 6.03.

*4.7.7. Reduction of the compounds **NO$_2$-2** and **NO$_2$-4**.* Firstly, 0.38 mmol of the corresponding nitro (**NO$_2$-2**, **NO$_2$-4**), 1.92 mmol of $SnCl_2 \cdot 2H_2O$, 20 mL of ethyl acetate and 5 mL of ethanol were placed into a round-bottomed flask equipped with a condenser. The mixture was refluxed for 4 h and the solution was cooled to room temperature, poured into 100 mL of ice/water and basified to pH 8 with NaOH aqueous solution (10%) under strong magnetic stirring for 2 h. The organic phase was extracted with $CH_2Cl_2$ (2×30 mL). The organic phases were combined and washed with NaOH

aqueous solution (5%, 1×100 mL) and water (2×100 mL). The organic phase was dried with anhydrous $Na_2SO_4$, the solvent removed and the crude product obtained was purified.

*4.7.8. 3,5-Bis(3-(4-(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl)aniline (**NH₂-2**).* The crude product was recrystallized once from butanone and once from 2-propanol, yielding 93% of white powder, mp 143.0 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3469, 3372, 2926, 2844, 1638, 1607, 1560, 1482, 1427, 1365, 1251, 1177, 841, 755. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 8.39 (s, 1H, Ar–H), 8.10 (d, 4H, *J*=8.9 Hz, Ar–H), 7.69 (s, 2H, Ar–H), 7.01 (d, 4H, *J*=8.9 Hz, Ar–H), 4.15 (br, 2H, Ar–$NH_2$), 4.03 (t, 4H, *J*=6.4 Hz, –$OCH_2$–), 1.82 (qt, 4H, *J*=6.4 Hz, –$OCH_2CH_2$–), 1.48 (qt, 4H, *J*=6.4 Hz, –$CH_2$–), 1.42–1.22 (br, 32H, –$CH_2$–), 0.88 (t, 6H, *J*=6.6 Hz, –$CH_3$). $^{13}$C NMR ($CDCl_3$), $\delta$, ppm: 174.7, 169.0, 161.9, 147.9, 129.3, 126.5, 119.1, 117.7, 117.5, 115.0, 68.4, 32.2, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.4, 26.3, 22.9, 14.4. Elemental analysis $C_{46}H_{63}N_5O_4$: required C, 73.66; H, 8.47; N, 9.34; Found: C, 73.55; H, 8.95; N, 9.29.

*4.7.9. 3,5-Bis(3-(3,4-bis(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl) aniline (**NH₂-4**).* The solid obtained was purified by column chromatography (silica gel, $CHCl_3$/EtOH 96:4), followed by recrystallization in butanone, yielding 90% of a light yellow solid, mp 131.1 °C (monotropic liquid crystal) I, –130.8 °C—$Col_h$, –98.7 °C—Cr. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3465, 3344, 2923, 2848, 1634, 1607, 1560, 1427, 1380, 1325, 1263, 1228, 1142, 755. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 8.41 (t, 1H, *J*=1.4 Hz, Ar–H), 7.76 (dd, 2H, *J*=8.5 Hz and *J*=1.9 Hz, Ar–H), 7.76 (d, 2H, *J*=1.4 Hz, Ar–H), 7.68 (d, 2H, *J*=1.9 Hz, Ar–H), 6.98 (d, 2H, *J*=8.5 Hz, Ar–H), 4.16 (br, 2H, Ar–$NH_2$), 4.12 (t, 4H, *J*=6.5 Hz, –$OCH_2$–), 4.08 (t, 4H, *J*=6.8 Hz, –$OCH_2$–), 1.89 (qt, 4H, *J*=6.5 Hz, –$OCH_2CH_2$–), 1.87 (qt, 4H, *J*=6.8 Hz, –$OCH_2CH_2$–), 1.52 (qt, 4H, *J*=6.5 Hz, –$CH_2$–), 1.50 (qt, 4H, *J*=6.8 Hz, –$CH_2$–), 1.43–1.21 (br, 64H, –$CH_2$–), 0.89 (t, 6H, *J*=6.6 Hz, –$CH_3$), 0.88 (t, 6H, *J*=6.8 Hz, –$CH_3$). $^{13}$C NMR ($CDCl_3$), $\delta$, ppm: 174.8, 169.2, 152.0, 149.4, 147.9, 126.5, 121.2, 119.3, 117.7, 117.6, 113.2, 112.3, 69.6, 69.3, 32.2, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.9, 14.4. Elemental analysis $C_{70}H_{111}N_5O_6$: required C, 75.16; H, 10.00; N, 6.27; found: C, 74.55; H, 9.85; N, 6.11.

*4.7.10. Deprotection of the compounds **OAc-2** and **OAc-4**.* The compounds **OAc-2** and **OAc-4** were not isolated. The reaction was performed as described in the general procedure for the synthesis of 1,2,4-oxadiazoles and the deprotection was performed in situ with 2 equiv of the $NaOH_{(aq)}$ and the solution was refluxed for 2 h. The mixture was then cooled to room temperature and poured into 200 mL of ice/water. The precipitate was filtered, washed with plenty of water, and purified.

*4.7.11. 3,5-Bis(3-(4-(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl)phenol (**OH-2**).* The solid obtained was recrystallized once over ethyl acetate and once over 2-propanol/acetonitrile affording 62% of a light brown solid, mp 121.5 °C (monotropic liquid crystal) I, –107.4 °C—$Col_h$, –61.8 °C—Cr. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3356, 2923, 2852, 1614, 1564, 1486, 1470, 1423, 1357, 1298, 1251, 1177, 919, 841, 763, 662. $^1$H NMR (Pyridine-$d_5$), $\delta$, ppm: 8.75 (s, 1H, Ar–H), 8.38 (d, 4H, *J*=9.0 Hz, Ar–H), 8.21 (s, 2H, Ar–H), 7.24 (d, 4H, *J*=9.0 Hz, Ar–H), 4.01 (t, 4H, *J*=6.6 Hz, –$OCH_2$–), 1.79 (qt, 4H, *J*=6.6 Hz, –$OCH_2CH_2$–), 1.47 (qt, 4H, *J*=7.4 Hz, –$CH_2$–), 1.35–1.26 (br, 32H, –$CH_2$–), 0.87 (t, 6H, *J*=7.4 Hz, –$CH_3$). $^{13}$C NMR (Pyridine-$d_5$), $\delta$, ppm: 175.4, 169.7, 162.6, 160.9, 130.1, 127.4, 120.0, 119.9, 118.9, 115.9, 68.9, 32.6, 30.4, 30.4, 30.4, 30.1, 30.10, 30.0, 26.8, 23.4, 14.8. Elemental analysis $C_{46}H_{62}N_4O_5$: required C, 73.57; H, 8.32; N, 7.46; found: C, 73.2; H, 8.50; N, 7.40.

*4.7.12. 3,5-Bis(3-(3,4-bis(dodecyloxy)phenyl)-1,2,4-oxadiazol-5-yl) phenol (**OH-4**).* The crude product was recrystallized once from 2-propanol and once from butanone, yielding 59% of a beige solid, mp (liquid crystal) 82.8 °C, $Col_h$ –184.6 °C. IR (KBr, $cm^{-1}$): $\nu_{max}$: 3407, 2923, 2848, 1607, 1564, 1489, 1466, 1443, 1384, 1349, 1267, 1220, 1148, 923, 799. $^1$H NMR (Pyridine-$d_5$), $\delta$, ppm: 8.79 (t, 1H, *J*=1.6 Hz, Ar–H), 8.56 (s, 1H, OH–Ar), 8.24 (d, 2H, *J*=1.6 Hz, Ar–H), 8.11 (dd, 2H, *J*=8.4 Hz and *J*=1.9 Hz, Ar–H), 8.06 (d, 2H, *J*=1.9 Hz, Ar–H), 7.24 (d, 2H, *J*=8.4 Hz, Ar–H), 4.11 (t, 8H, *J*=6.3 Hz, –$OCH_2$–), 1.88 (m, 8H, –$OCH_2CH_2$–), 1.56 (m, 8H, –$CH_2$–), 1.41–1.21 (br, 64H, –$CH_2$–), 0.90 (t, 12H, *J*=6.3 Hz, –$CH_3$). $^{13}$C NMR (Pyridine-$d_5$), $\delta$, ppm: 175.6, 170.0, 160.8, 153.4, 127.6, 122.3, 120.4, 120.2, 119.0, 114.7, 113.9, 70.3, 70.0, 32.6, 30.5, 30.4, 30.4, 30.4, 30.3, 30.2, 30.2, 30.1, 27.0, 26.9, 23.4, 23.4, 14.7, 14.7. Elemental analysis $C_{70}H_{110}N_4O_7$: required C, 75.09; H, 9.90; N, 5.00; found: C, 74.70; H, 10.10; N, 5.00.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.10.019.

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