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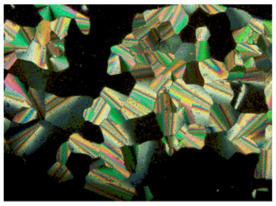
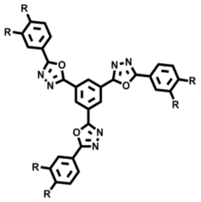
Edivandro Girotto[a], Juliana Eccher[b], André A. Vieira[a], Ivan H. Bechtold[b] and Hugo Gallardo[a,*]
[a]*Departamento de Química Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*
[b]*Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*





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

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[a]*Departamento de Química Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*
[b]*Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*

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ABSTRACT

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

Introduction

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

Liquid crystals offer many possibilities for their functionalization through hydrogen bonds leading to self-organized systems[8], arrangements with strong π-conjugation, which may promote luminescence, and the introduction of heterocyclic groups, which have a strong influence on their physical properties and mesomorphic behavior[9]. Liquid crystals incorporating the 1,3,4-oxadiazole heterocycle have received significant attention since the first reports of their mesomorphic properties[10]. They have become good candidates for application in organic electronics[11] due to high fluorescence quantum yields, charge carrier mobility and good chemical and thermal stability[12]. Thus, in recent years, various liquid crystals based on different molecular shapes, such as rod-like[13], dimers[14], polymers[15], 1,3,4-oxadiazole-based polycatenar[16], and star-shaped[17], and also bent-core LCs, have been reported[18]. Oxadiazole molecules are among the most widely investigated as electroluminescent materials and as electron-transport materials in OLEDs[15], where a series of compounds containing the 1,3,4-oxadiazole ring, such as the compound 2,5-bis(4-naphthyl)-1,3,4-oxadiazole, has become one of the top organic electron conductors[16].

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

Experimental Section

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

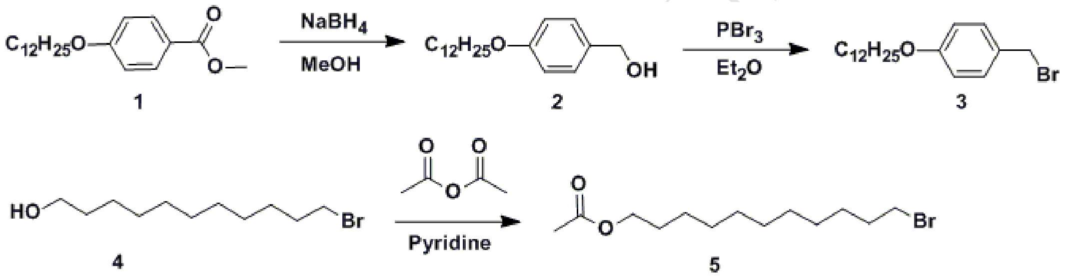
The textures of the mesophases were captured with polarizing optical microscopy (POM) using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage and a PM-30 exposure control unit. Thermal transitions and enthalpies were determined by differential scanning calorimetry (DSC) using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

The X-ray diffraction (XRD) experiments were carried out on an X`Pert-PRO (PANalytical) diffractometer using the linear monochromatic Cu Kα beam (ʎ = 1.5405 Å), with an applied power of 1.2 kVA. The samples were prepared using procedures described in the literature[19] with the heating and cooling of an amount of powder on glass plates. The scans were performed in continuous mode from 2^o to 30^o (2θ angle) with the samples in the mesophase, obtained by cooling from the isotropic state. The absorption spectra in solution were obtained with an HP UV-Vis model 8453 spectrometer. The fluorescence spectra in solution were recorded on a Hitachi-F-4500.

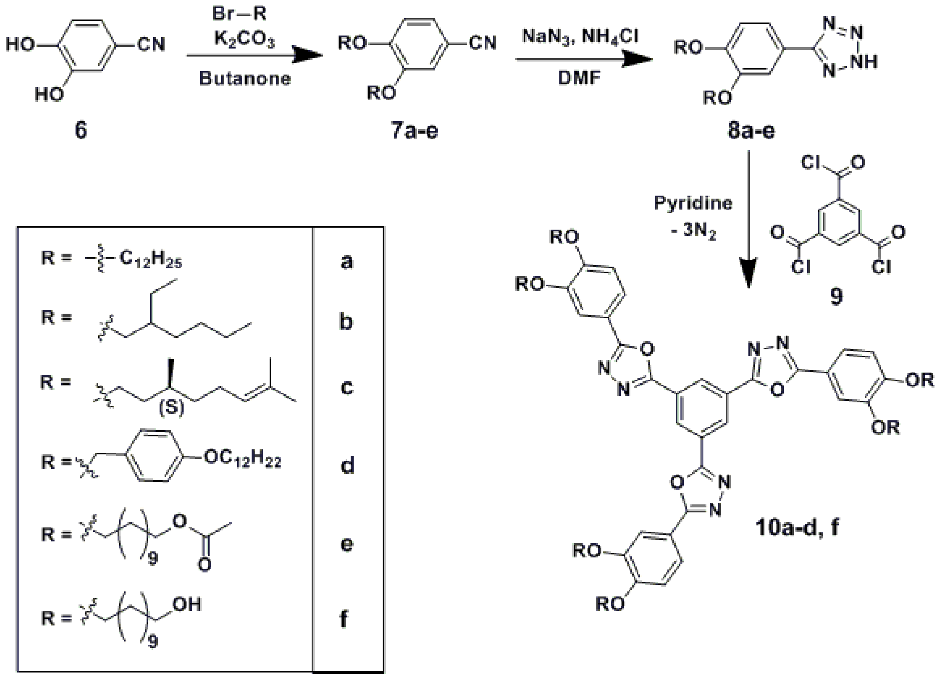
The relative fluorescence quantum yields (ΦFl) were determined according to a published method[20]. The absorption and fluorescence measurements for thin solid films were collected on an OceanOptics (USB4000) spectrophotometer.

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

Cyclic voltammetry analysis was performed to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). A three-electrode cell was used, comprised of a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag$^+$/AgCl electrode as the reference and the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple as an internal standard. Before each measurement, the cell was deoxygenated by purging with nitrogen. Electrochemical measurements, using cyclic voltammetry, were performed on an Autolab PGSTAT128N potentiostat/galvanostat (Eco Chemie, The Netherlands) connected to data processing software (GPES, software version 4.9.007, Eco Chemie).



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



Scheme 2. Synthesis of target compounds **10a-d, f**.

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

The synthetic route adopted for the preparation of the final compounds derived from 1,3,4-oxadiazole heterocyclic is shown in **Scheme 2**. Initially, with compound **6**, alkylation reactions were carried out using different bromides **3**, **5**, 1-bromoundecane, 3-(bromomethyl)heptane and (*S*)-8-bromo-2,6-dimethyloct-2-ene and employing potassium carbonate and butanone under reflux[8]. After obtaining the nitriles **7a-e**, these compounds were reacted with sodium azide and ammonium chloride in DMF to generate the corresponding tetrazoles **8a-e** through the Tiemann reaction[21]. Following the synthetic route, the benzene-1,3,5-tricarboxylic acid was converted to its corresponding acid chloride with thionyl chloride and then immediately reacted with the tetrazoles **8a-e** in dry pyridine under reflux to afford the final compounds **10a-d**. The reaction applied to obtain the heterocyclic 1,3,4-oxadiales is followed by the intense liberation of nitrogen gas, which is characteristic of the Huisgen reaction[22]. The **10e** molecule, with the acetyl group, was not isolated. After preparation, this compound was directly deprotected, remaining six free hydroxyl groups at the end of the alkyl chain. The hydrolysis reaction was carried out using sodium hydroxide in $EtOH/H_2O$ to obtain the respective compound **10f**. All compounds synthesized were characterized by ^1H and ^{13}C NMR and IR spectroscopy. Also, the final compounds were characterized by MALDI-MS (see supporting information).

Results and discussion

Mesomorphic Properties. The phase transition temperatures of all of the compounds (**10a–d, f**) were initially established by POM and then accurately measured by DSC. The DSC results with their associated enthalpy changes are given in **Table 1**. The thermal parameters are taken from the first heating−cooling cycles of DSC scans. With the exception of **10f**, all compounds exhibited mesomorphic behavior, exclusively hexagonal columnar (Col_h), identified by the typical optical textures, where on cooling a dendritic growth from the isotropic liquid and a combination of mosaics with linear and fan shaped birefringent defects, together with homeotropic regions, were observed through POM, as seen in **Figure 1**. The Col_h mesophases were later confirmed via XRD experiments. Compound 1**0f** did not show liquid crystalline phases, it melted directly into the isotropic liquid state at 109-110 °C, and on cooling, the sample crystallizes. The lack of mesomorphism is probably due to the free hydroxyl group at the end of the alkyl chain, which hinders the mesomorphic behavior even for a stable columnar liquid crystal[23].Using the same number of substituents but with different alkoxy chains a considerable variation was observed in the thermal behavior of the respective liquid-crystalline materials. Compound **10b** with branched chains, compared with **10a** which contains 12 carbon atoms in a straight chain, showed the lowest melting point at 81 °C and the lowest mesomorphic range of the series (Δ = 52.4°C). Furthermore, compounds **10a** and **10b** showed crystallization on cooling to 77.7 °C and 38.2 °C, respectively. The compound **10c** shows only one transition (Col_h–I) at 116.1 °C during heating and one transition (I–Col_h) at 104.9 °C during cooling, which is the widest mesophase range amongst all derivatives synthesized in this work. The enthalpy values from the columnar to isotropic phase of the compounds **10a-d** were between ΔH = 1.5-7.6 kJ/mol and suggest a high mesophase stability, based on the existence of strong interdisc core-core π interactions. Comparing the transition temperatures of compounds **10a**, **10b** and **10c** reveals that it is possible to modulate the mesomorphic range of the same columnar phase simply by using different terminal alkyl chains (straight and branched).

The molecule **10d**, containing 4-dodecyloxybenzyl groups as substituents, does not present crystallization on cooling cycle. On microscope, this compound shows liquid-crystalline behavior at room temperature, but does not present any characteristic texture itself. When cooled down from the isotropic liquid, it shows characteristic broken fan and mosaic textures of discotic columnar phases. The DSC thermogram displays two soft solid transitions followed by another one representing the transition from columnar phase to isotropic liquid on heating. Upon cooling, it shows only the transition from isotropic liquid to columnar phase, remaining stable in this phase until room temperature.

The thermal stability of the final compounds **10a-d** and **10f** was studied by TGA under nitrogen atmosphere. Compound **10d** showed decomposition onset at 368 °C while for all of the other compounds the corresponding temperature was above 400 °C (see supporting information).

Figure 1. Optical photomicrographs of different col_h phases under crossed polarizers: (a) focal conic for **10a** at 151 °C, (b) pseudo focal conic for **10b** at 90 °C, (c) mosaic textural pattern for **10c** at 25 °C and (d) rectilinear defects for **10d** at 172 °C.

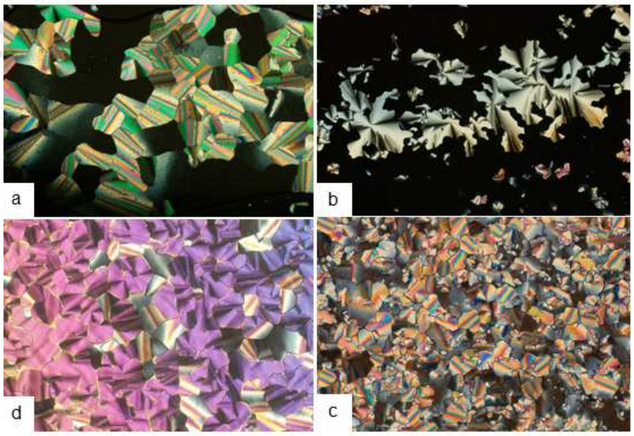


Table 1. Phase transitions and enthalpies (kJ/mol) of compounds **10a-d**.

Compound	Phase transition profile[a]	XRD data T (°C)	 *a*[b] (Å)
10a	Cr 103.1 (54.4) Col_h 183.7 (3.9) I I 181.0 (5.6) Col_h 77.7 (5.6) Cr	170	35.9
10b	Cr 81.1 (6.4) Col_h 108.3 (1.9) I I 90.6 (1.3) Col_h 38.2 (0.7) Cr	90	28.1
10c	Col_h 116.1 (1.5) I I 104.9 (0.9) Col_h[c]	30	31.2
10d	ss 78.0 (0.4) ss 132.0 (3.1) Col 235.7 (8.4) I I 231.8 (7.6) Col_h[c]	120	47.9

Transition temperatures (°C) and in parentheses the transition enthalpies (kJ/mol), determined by DSC during heating (first line) and cooling (second line) cycles. ss = soft solid; Cr = crystalline; Col_h = columnar hexagonal; I = isotropic liquid. [b]Intercolumnar distance. [c] The Col_h phase did not crystallize upon cooling down to −50 °C.

X-ray diffraction studies. The molecular organization observed by POM was confirmed by XRD experiments for compounds **10a-d** and the diffraction peaks indexed by the Miller indices. All of the compounds presented an intense diffraction peak at the low angle region (100) and some of them also showed peaks at 110 and 200. It is well known that for col$_h$ phases the ratio between these peaks should be1: √3: √4[23], as demonstrated here in. In addition, a diffuse peak relative to the liquid-like order of the peripheral alkoxybenzyl groups was observed at around 4.6 Å and the peak at around 3.4 Å indicates a periodic intracolumnar spacing between neighboring discs. This is of particular interest for electronic applications due to the close π-staking[2c,24] and contributes to the stability of the mesophase. In **Figure 2**, the XRD spectrum of compound **10c** at 30 °C shows that the hexagonal order is preserved until room temperature without crystallization. The XRD spectra of the other mesomorphic compounds are presented in the supporting information, together with the lattice parameters.

The intercolumnar distances (a) presented in **Table 1** were obtained from XRD data according to reports in the literature[25]. The molecular diameters of compounds **10a**, **10b**, **10c** and **10d** (47.5 Å, 31.9 Å, 37.7 Å and 55.8 Å) were estimated using ChemBio3D Ultra Software, version 11.0.1.The fact that these values are between 11.6 Å and 3.8 Å (for compounds **10a** and **10b**, respectively) larger than a suggest that all of the compounds present interdigitation of the alkoxy chains or non linear conformations. This may explain the reason why compound **10e** does not present mesomorphic behavior. The OH groups at the end of aliphatic chains probably form hydrogen bonds with the terminal OH groups, which prevents interdigitation of the chains and consequently the columnar phase.

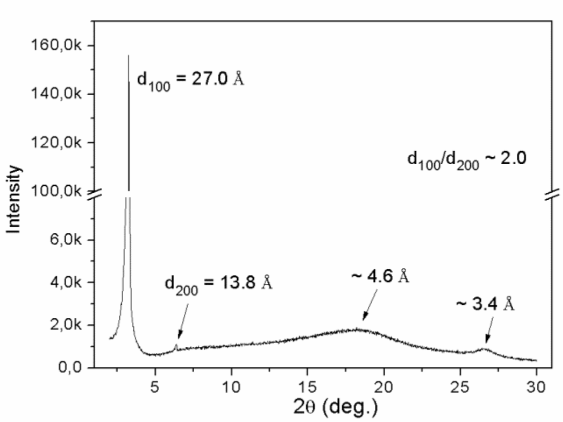


Figure 2. XRD pattern obtained for compound **10c** in the Col$_h$ phase at 30 °C.

Optical Properties. The UV–Vis absorption and fluorescence spectra of **10a-d, f** in chloroform solution are presented in **Figure 3** and the data are summarized in **Table 2**. As expected, the changing of the alkoxy chains did not affect the electronic properties of these materials, and the absorption and emission spectra show similar profiles. The maximum absorption wavelength (ʎ máx) of the final compounds in solution varied from 323 to 329 nm. These compounds presented a strong blue emission under UV-light with maxima at around 410 nm. These materials exhibited good quantum yields of between 0.47-0.63 in relation to quinine sulfate[26].The high molar absorption coefficient (□ ≈ 47.000L mol^{-1} cm^{-1}) for these compounds is attributed to the π−π* transitions from the heterocyclic 1,3,4-oxadiazole portion[17, 27].The Stokes shift for these molecules is approximately 84 nm in solution.

Cyclic voltammetry measurements were performed on compound **10c**, which presents an enantiotropic col$_h$ mesophase which is preserved until room temperature during cooling. This characteristic is important for practical applications in electronics, where annealing processes can be used to obtain macroscopic molecular ordering. Based on the optical band gap obtained from the absorption spectrum (E_{gap} = 3.80 eV) it was possible to determine the HOMO = -5.21 eV and LUMO = -1.41 eV electronic orbitals (for more details see supporting information).

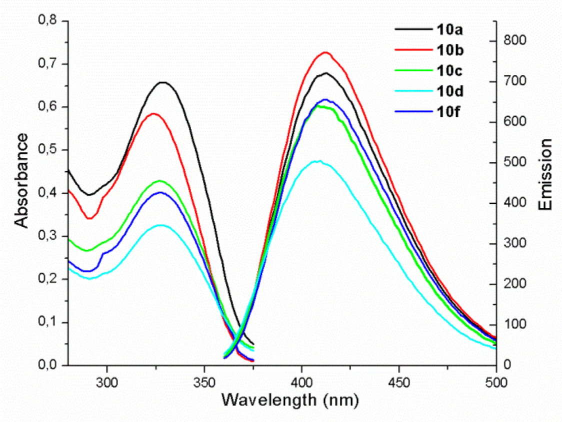


Figure 3. Optical absorption and fluorescence spectra obtained for the final compounds **10a-e**, in chloroform solution (10^{-5} M).

Table 2. Optical data for compounds **10a-d, f** in chloroform solution (10^{-5} M).

Compound	Absorption[a]	Emission[b]	Stokes Shift	ϕ_F[c]
10a	327	413	86	0.57
10b	329	411	82	0.63
10c	326	410	84	0.59
10d	323	406	83	0.47
10f	327	411	84	0.55

[a] 10^{-5} M in chloroform at 20 °C, [b] Excitation wavelength at λ max of absorption, [c] Quantum yield relative to quinine sulfate.

The photophysical properties of these compounds were also studied in solid films. The maximum absorption wavelengths of compounds **10c-d** are blue-shifted compared to those in solution, as is commonly observed for thin solid films[28,29], but without significant changes in the shape of the absorption spectra. On the other hand, for compounds **10a,b** the wavelength of maximum absorption was preserved but with the appearance of a shoulder at lower wavelengths (see supporting information). The emission was captured as a function of the temperature using the same samples employed in the XRD analysis. All final compounds displayed strong luminescence in the range of 400-550 nm when excited with UV-light, most of them demonstrating bathochromic shifts compare to the emission in solution. The emission spectra for compound **10b** as a function of the temperature are shown in **Figure 4a**. Several spectra were collected by heating the sample from the crystal to the isotropic phase. Changes in the shape of the profile are commonly observed and are well described in the litterature[24]. The diminution in the maximum emission intensity on increasing the temperature (see **Figure 3b**) is expected for semiconducting materials and is associated with thermally activated non-radioactive decay processes[23, 30]. Compounds **10a**, **10c** and **10d** presented similar behavior (see supporting information).

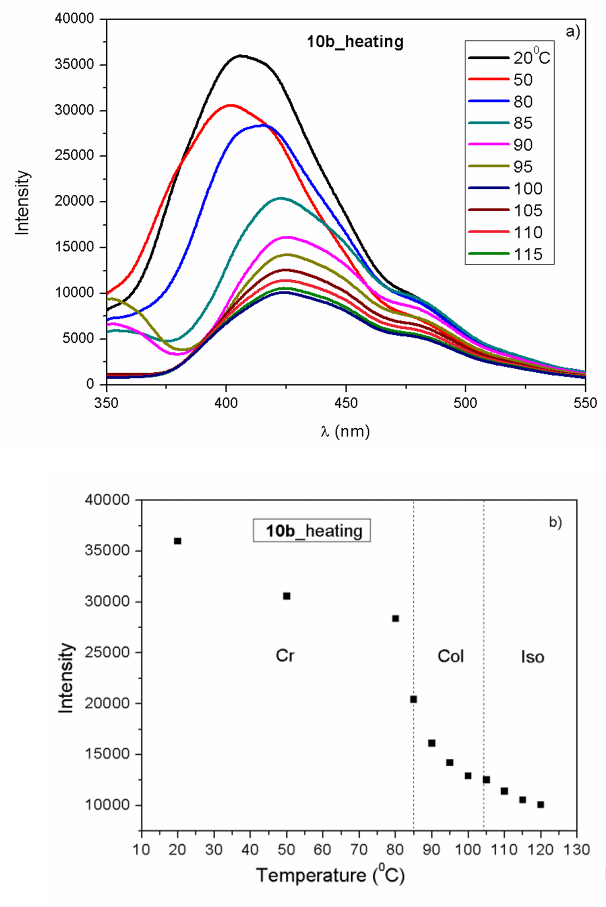


Figure 4. a) Emission spectra of compound **10b** recorded during heating from crystal to the isotropic phase. (b) Maximum intensity as a function of the temperature.

Conclusions

A new series of compounds derived from the 1,3,4-oxadiazole heterocyclic was designed and synthesized. Four compounds presented liquid crystalline properties with hexagonal columnar mesomorphism and good thermal stability. The mesomorphic properties are closely dependent on the aliphatic chains connected to the rigid disc-like core (their chirality and the presence of OH groups). For compounds **10c** and **10d** the hexagonal columnar phase was preserved until room temperature with no evidence of crystallization. All of them presented intense blue photoluminescence in solution and in solid films. These characteristics together with the strong overlapping π molecular orbitals make these materials good candidates for applications in organic electronic devices.

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Tables

Table 1. Phase transitions and enthalpies (kJ/mol) of compounds **10a-d**.

		XRD data	
Compound	Phase transition profile[a]	T (ºC)	a[b] (Å)
10a	Cr 103.1 (54.4) col$_h$ 183.7 (3.9) I I 181.0 (5.6) col$_h$ 77.7 (5.6) Cr	170	35.9
10b	Cr 81.1 (6.4) col$_h$ 108.3 (1.9) I I 90.6 (1.3) col$_h$ 38.2 (0.7) Cr	90	28.1
10c	col$_h$ 116.1 (1.5) I I 104.9 (0.9) col$_h$[c]	30	31.2
10d	ss 78.0 (0.4) ss132.0 (3.1) Col 235.7 (8.4) I I 231.8 (7.6) Col$_h$[c]	120	47.9

Transition temperatures (°C) and in parentheses the transition enthalpies (kJ/mol), determined by DSC during heating (first line) and cooling (second line) cycles. ss = soft solid; Cr = crystalline; col$_h$ = columnar hexagonal; I = isotropic liquid. [b]Intercolumnar distance. [c] The Col$_h$ phase did not crystallize upon cooling down to −50 °C.

Table 2. Optical data for compounds **10a-e** in chloroform solution (10^{-5} M).

Compound	Absorption[a]	Emission[b]	Stokes Shift	ϕ_F[c]
10a	327	413	86	0.57
10b	329	411	82	0.63
10c	326	410	84	0.59
10d	323	406	83	0.47
10e	327	411	84	0.55

[a] 10^{-5} M in chloroform at 20 °C, [b] Excitation wavelength at λ max of absorption, [c] Quantum yield relative to quinine sulfate.

Legends for Figures

Figure 1. Optical photomicrographs of different col$_h$ phases under crossed polarizers: (a) focal conic for **10a** at 151 °C, (b) pseudo focal conic for **10b** at 90 °C, (c) mosaic textural pattern for **10c** at 25 °C and (d) rectilinear defects for **10d** at 172 °C.

Figure 2. XRD pattern obtained for compound **10c** in the Col$_h$ phase at 30 °C.

Figure 3. Optical absorption and fluorescence spectra obtained for the final compounds **10a-d, f**, in chloroform solution (10^{-5} M).

Figure 4. a) Emission spectra of compound **10b** recorded during heating from crystal to the isotropic phase. (b) Maximum intensity as a function of the temperature

Legends for Schemes

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

Scheme 2. Synthesis of target compounds **10a-d, f**.

Supporting Information

Luminescent Columnar Liquid Crystals Based on 1,3,4-oxadiazole

Edivandro Girotto[a], Juliana Eccher[b], André A. Vieira[a], Ivan H. Bechtold[b] and Hugo Gallardo[a,*]

[a]*Departamento de Química Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*
[b]*Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis-SC, 88040-900, Brazil.*

*Email: hugo@qmc.ufsc.br; fax: +55 48 37216850; tel: +55 48 37219544

Experimental

Methyl *p*-(dodecyloxy)benzoate (1). 4.0 g (26 mmol) of methyl 4-hydroxybenzoate, 7.17 g (52 mmol) of K_2CO_3, 7.17 g (29 mmol) of 1-bromododecane and 150 mL of butanone were refluxed for 24h. The suspension was filtered and washed twice with hot butanone. The solvent was removed by rotary evaporation and the solid was recrystallized with ethanol and water, resulting in 7.5 g of a white solid. Yield 90%. Mp: 54.0-56.2 ^{o}C. IR (KBr pellet) ν_{max}cm^{-1}: 2955, 2849, 1725, 1609.^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.98 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.9 Hz, 2H, Ar-H), 4.0 (t, *J* = 6.4 Hz, 2H, O-CH_2), 3.88 (s, 3H, -COO-CH_3),1.79 (m, 2H, -CH_2),1.43 (m, 2H, -CH_2), 1.26 (m, 16H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3).^{13}C NMR ($CDCl_3$), δ, ppm: 166.9, 131.5, 122.3, 114.0, 68.2, 51.8, 31.9, 29.6, 29.6, 29.6, 29.4, 29.1, 22.7, 14.1.

***p*-(Dodecyloxy)benzylalcohol (2).** Under argon atmosphere, 1.4 g (34 mmol) of $LiAlH_4$ was added in 100 mL of dry THF and the mixture was cooled to -5 ^{o}C. Compound **1** (7.30 g (23 mmol)) was dissolved in 70 mL of dry THF, and added slowly dropwise for 1h. Then, the solution temperature was raised until room temperature and kept steering for more 3h. 30 mL of ethanol was carefully added dropwise in the reaction and the solvent removed by rotary evaporation. The solid was dissolved in ethyl acetate and the white suspension was filtrated. The solvent was removed by rotary evaporation and 6.0 g of a white solid was obtainded. Yield 90%. Mp: 65.2-67.0 °C. IR (KBr pellet) ν_{max}cm^{-1}: 3322, 2955, 2849, 1614, 1584. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.28 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.61 (s, 2H, -CH_2-OH), 3.95 (t, *J* = 6.5 Hz, 2H, -O-CH_2), 1.78 (m, 2H, -CH_2), 1.45 (m, 2H, -CH_2), 1.26 (m, 16H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3).^{13}C NMR ($CDCl_3$), δ, ppm: 158.8, 132.8, 128.8, 114.5, 68.0, 65.1, 31.9, 29.7 29.6, 29.6, 29.4, 29.2, 26.0, 22.7, 14.1.

1-(Bromomethyl)-4-(dodecyloxy)benzene (3). A solution of 7.7 g (21 mmol) of compound **2** in 20 mL of 48% bromic acid and 20 mL of THF was stirred at room temperature for 3h. The resulting solution was extracted with chloroform (3 x 40 mL). The separated organic phase was washed with saturated aqueous $NaHCO_3$, dried with $CaCl_2$ and the solvent was removed by rotary evaporation to give 7.4 g of compound **3**. Yield 96%. Mp: 40.0-43.0 °C. IR (KBr pellet) ν_{max} cm^{-1}: 2953, 2918, 2849, 1609. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.31 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.85 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.50 (s, 2H, Ar-CH_2-Br), 3.95 (t, *J* = 6.4 Hz, 2H, O-CH_2), 1.77 (m, 2H, -CH_2), 1.44 (m, 2H, -CH_2), 1.27 (m, 16H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 159.2, 130.4, 129.6, 114.7, 68.1, 34.1, 31.9, 29.6, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 14.1.

11-Bromoundecyl acetate (5). A solution of 3.0 g (12 mmol) of 11-bromoundecan-1-ol, 4 mL (42 mmol) of pyridine and 4 mL (42 mmol) of acetic anhydride was refluxed for 3h. The solution was then added in 150 mL of water/ice, acidified to pH 2 with HCl aqueous solution (15%). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 x 40 mL), and dried with anhydrous Na_2SO_4. The organic solvent was removed by rotary evaporation and 3.4 g of a colorless oil was obtained. Yield 97%. IR (KBr pellet) ν_{max}cm^{-1}: 2927, 2855, 1740.^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 4.01 (t, J = 6.8 Hz, 2H, -COO-CH_2), 3.36 (t, *J* = 6.8 Hz, 2H, Br-CH_2), 2.00 (s, 2H, -$COOCH_3$), 1.81, 1.57, 1,38 (m, 6H, -CH_2), 1.24 (m, 14H, -CH_2). ^{13}C NMR ($CDCl_3$), δ, ppm: 187.4, 171.4, 64.8, 34.2, 33.0, 29.6, 29.6, 29.6, 29.4, 29.0, 28.8, 28.4, 26.1.

3,4-Bis(dodecyloxy)benzonitrile (7a). 3.0 g (22 mmol) of compound **6**, 15.3 g (111 mmol) of K_2CO_3, 12.1 g (49 mmol) of 1-bromododecane, 0.4 g (1 mmol) of TBAB and 150 mL of butanone were refluxed for 24h. The suspension was filtered and washed twice with hot butanone. The solvent was removed by rotary evaporation and the solid recrystallized with ethanol and water, and a 9.2 g of a white solid was obtained. Yield

89%. Mp: 75-81 ^{o}C. IR (KBr pellet) ν_{max}cm^{-1}: 2955, 2917, 2850, 2873, 2850, 2221, 1597. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.24 (dd, *J* = 8.2, 1.7 Hz, 1H, Ar-H), 7.02 (d, *J* = 1.7 Hz, 1H, Ar-H), 6.87 (d, *J* = 8.2 Hz, 1H, Ar-H), 4.50 (t, *J* = 6.2, 2H, OCH_2), 3.98 (t, *J* = 6.6 Hz, 2H, O-CH_2), 1.83 (m, 4H, -CH_2), 1.46 (m, 4H, -CH_2), 1.27 (m, 32H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 6H, -CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 153.02, 149.0, 126.2, 119.4, 115.9, 112.6, 103.4, 69.3, 69.0, 31.9, 29.6, 29.6, 29.5, 25.6, 29.3, 28.9, 22.6, 14.1.

3,4-Bis(2-ethylhexyloxy)benzonitrile (7b). The same procedure used to obtain compound **7a** was applied. The compound was purified by column chromatography using hexane/ethyl acetate (80:20) as the eluent, resulting in 2.5 g of an oil. Yield 89%. IR (KBr pellet) ν_{max}cm^{-1}: 2958, 2926, 2877, 2225, 1598.^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.23 (dd, *J* = 8.4, 1.5 Hz, 1H, Ar-H), 7.06 (d, *J* = 1.6 Hz, 1H, Ar-H), 6.87 (d, *J* = 8.4 Hz, 1H, Ar-H), 3.90 (m, 4H, O-CH_2), 1.75 (m, 2H, -CH), 1.48 (m, 8H, -CH_2), 1.31 (m, 8H, -CH_2), 0.93 (m, 12H, -CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 153.4, 149.4, 126.1, 119.5, 115.6, 112.4, 103.3, 71.6, 71.3, 39.3, 30.5, 29.0, 23.9, 23.0, 14.0, 11.1.

3,4-Bis((*S*)-3,7-dimethyloct-6-enyloxy)benzonitrile (7c). The same procedure used to obtain compound **7a** was applied. The compound was purified by column chromatography using hexane/ethyl acetate (95:5) as the eluent, resulting in 2.4 g of an oil. Yield 96%. IR (KBr pellet) ν_{max}cm^{-1}: 2964, 2926, 2877, 2224, 1598. (400 MHz, $CDCl_3$), δ, ppm: 7.24 (dd, *J* = 8.4, 1.8 Hz, 1H, Ar-H), 7.07 (d, *J* = 1.8 Hz, 1H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 1H, Ar-H), 5.09 (m, 2H, CH), 4.06-4.01 (m, 4H, O-CH_2), 2.00-1.88 (m, 8H, -CH_2), 1.68-1.60 (m, 12H, -CH_3), 1.39-1.25 (m, 6H, -CH_2), 0.97-95 (m, 6H, -CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 153.0, 149.0, 126.3, 124.6 119.5, 115.8, 112.6, 103.5, 67.6, 67.4, 37.1, 35.8, 29.6, 25.7, 19.6, 17.7.

3,4-Bis(4-(dodecyloxy)benzyloxy)benzonitrile (7d). The same procedure used to obtain compound **7a** was applied. The crude solid was purified and recrystallized in ethanol, resulting in 6.2 g of a yellow solid. Yield 88%. Mp: 124-127 ^{o}C. IR (KBr pellet) ν_{max}cm^{-1}: 2954, 2920, 2850, 2219, 1615. (400 MHz, $CDCl_3$), δ, ppm: 7.31 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 2H, Ar-H), 7.13 (d, *J* = 1.9 Hz, 2H, Ar-H), 6.94 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.89 (d, *J* = 8.4 Hz, 4H, Ar-H), 5.11 (s, 2H, Ar-CH_2),), 5.06 (s, 2H, Ar-CH_2), 3.95 (m, 4H, O-CH_2), 1.78 (m, 4H, -CH_2), 1.48 (m, 4H, -CH_2), 1.26 (m, 28H, -CH_2), 0.88 (m, J = 6.8, 6H, -CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 159.2, 152.9, 148.8, 129.0, 128.9, 127.9, 127.7, 126.7, 119.2, 117.8, 114,6, 114.1, 104.0, 71.3, 152.9, 148.8, 129.0, 128.9, 127.9, 127.7, 126.7, 119.2, 117.46, 114.6, 104.0, 71.3, 70.8, 68.0, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1.

11,11'-(4-Cyano-1,2-phenylene)bis(oxy)bis(undecane-11,1-diyl) diacetate (7e). The same procedure used to obtain compound **7a** was applied. The solid was purified by column chromatography using CH_2Cl_2/ethanol (97:3) as the eluent, resulting in 1.8 g of a yellow solid. Yield 73%. Mp: 108-111 ^oC. IR (KBr pellet) $\nu_{max}cm^{-1}$: 2916, 2870, 2850, 2220, 1742, 1597. (400 MHz, $CDCl_3$), δ, ppm: 7.24 (dd, *J* = 8.3, 1.8 Hz, 1H, Ar-H), 7.06 (d, *J* = 1.8 Hz, 1H, Ar-H), 6.8 (d, *J* = 8.3 Hz, 1H, Ar-H), 4.05 (s, 4H, COO-CH_2), 3.98 (m, 4H, O-CH_2), 2.04 (s, 4H, -CH_3), 1.83 (m, 4H, -CH_2), 1.46 (m, 4H, -CH_2), 1.28 (m, 30H, -CH_2). ^{13}C NMR ($CDCl_3$), δ, ppm: 171.5, 153.2, 119.2, 126.5, 119.7, 116.2, 112.9, 103.7, 69.6, 69.3, 66.9, 29.7, 29.6, 29.5, 29.2, 29.2, 28.8, 26.1, 21.3.

***General procedure for the synthesis of compounds* (8a-e).** 8g (17 mmol) of compound **7a**, 4.4 g (68 mmol) of NaN_3 and 3.6 g (68 mmol) in 70 mL DMF were refluxed for 24h. The suspension was cooled to room temperature and poured in 300 mL of ice/water and acidified to pH 2 with HCl aqueous solution (15%). The solid was filtrated and washed with water and recrystallized in *iso*-propanol, resulting in 7.6 g of compound **8a**.Yield 87%. Mp: 157 ^oC. IR (KBr pellet) $\nu_{max}cm^{-1}$: 2921, 2850, 2800-2500, 1609. ^1H NMR (400 MHz, Pyridine-d_6 (90 ^0C), δ, ppm. 8.01 (s, 1H, Ar-H), 7.99 (s, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 4.39 (t, 2H, O-CH_2), 3.99 (t, 2H, O-CH_2), 1.82 (m, 2H, -CH2-), 1.50 (m, 2H, -CH2-), 1.27 (m, 36H), 0.80 (m, 6H, CH_3, CH2). ^{13}C NMR (Pyridine-d_6 (90 ^0C)), δ, ppm: 157.9, 152.4, 121.3, 118.8, 114.5, 113.1, 69.7, 32.6, 30.1, 29.9, 23.4, 14.8.

5-(3,4-Bis(2-ethylhexyloxy)phenyl)-2*H*-tetrazole (8b). The oil was purified by column chromatography using hexane/ethyl acetate (95:5) as the eluent, resulting in 1.8 g of **8b**. Yield 92%. IR (KBr pellet) $\nu_{max}cm^{-1}$: 2966, 2916, 2876, 1609, 1516. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.66 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 6.90 (d, *J* = 8.2 Hz, 1H, Ar-H), 3.84 (s, 4H, O-CH_2), 1.75, 1.69 (m, 2H, -CH_2), 1.43 (m, 4H, -CH_2),1.29, 1.25 (m, 12H, -CH_2), 0.93, 0.84 (mt, 12H, -CH_3); ^{13}C NMR ($CDCl_3$), δ, ppm: 153.3, 150.0, 120.5, 115.5, 112.6, 111.6, 105.0, 71.4, 39.4, 30.5, 29.1, 23.8, 23.0, 14.0, 11.1.

5-(3,4-Bis((*S*)-3,7-dimethyloct-6-enyloxy)phenyl)-2*H*-tetrazole (8c). This compound was obtained as a white solid and no purification was required. Yield 88%. Mp: 86-88 ^oC.

IR (KBr pellet) $\nu_{max}cm^{-1}$: 2966, 2916, 2993, 2639, 1609. ^{1}H NMR (400MHz, CDCl$_3$), δ, ppm: 7.69 (d, *J* = 8.2 Hz, 1H, Ar-H),7.68 (s, 1H, Ar-H), 6.96 (d, *J* = 8.2 Hz, 1H, Ar-H), 5.07 (m, 2H, =CH), 4.06 (s, 4H, O-CH$_2$),1.95, 1.85 (m, 4H, -CH$_2$),1.65, 1.57 (m, 12H, -CH$_3$), 1.36, 1.19 (m, 10H, -CH$_2$), 0.95, 0.90 (m, 6H, -CH$_3$). ^{13}C NMR (CDCl$_3$), δ, ppm: 151.9, 149.6, 131.3, 131.2, 126.6, 120.7, 115.5, 113.1, 111.9, 67.5, 37.2, 36.0, 29.7, 25.7, 25.5, 19.5, 17.6.

5-(3,4-Bis(4-(dodecyloxy)benzyloxy)phenyl)-2*H*-tetrazole (8d). The compound was recrystallized in ethanol and a light brown solid was obtained. Yield 91%. Mp: 137-139 124-127 °C. IR (KBr pellet) $\nu_{max}cm^{-1}$: 3076, 2955, 2919, 1850, 2734-2481, 1610. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 7.66 (s, 1H, Ar-H), 7.53 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.30 (d, *J* = 8.6 Hz, 4H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.83 (dd, *J* = 8.6 Hz, 4H, Ar-H), 5.10 (s, 4H, Ar-CH$_2$), 3.92 (m, 4H, O-CH$_2$), 1.76, 1.45 (m, 8H, -CH$_2$), 1.26 (m, 32H, -CH$_2$), 0.87 (m, 6H, -CH$_3$). ^{13}C NMR (CDCl$_3$), δ, ppm: 159.2, 152.9, 148.8, 129.0, 124.7, 126.7, 119.2, 117.8, 114.6, 114.2, 104.0, 71.3, 70.8, 68.0, 31.9, 29.7 29.6, 29.4, 29.3, 29.2, 26.0, 22.3, 14.1.

11,11'-(4-(2*H*-tetrazol-5-yl)-1,2-phenylene)bis(oxy)diundecan-1-ol (8e). The compound was purified by column chromatography using dichloromethane as eluent and a light brown solid was obtained. Yield 73%. Mp: 108-110 °C. IR (KBr pellet) $\nu_{max}cm^{-1}$: 3452, 3073, 2921, 2849, 2745-2485, 1741,1607. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 7.67 (sl, 2H, Ar-H), 6.9 (d, *J* = 8.0 Hz, 1H, Ar-H), 4.05 (s, 8H, O-CH$_2$), 2.07 (s, 6H, -COOCH$_3$), 1.81, 1.61, 1,43 (m, 12H, -CH$_2$), 1.27 (m, 24H, -CH$_2$). ^{13}C NMR (CDCl$_3$), δ, ppm: 171.8, 171.7, 151.7, 149.4, 126.2, 120.5, 115.9, 113.2, 112.1, 69.0, 64.8, 33.0, 32.7, 24.4, 29.3, 29.1, 29.0, 28.8, 28.5, 28.4, 28.1, 25.8, 25.7, 21.0, 20.9.

General procedure for the synthesis of target compounds 10a-d.

1,3,5-Tris-(5-(3,4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl)benzene (10a). 1,3,5-benzenetricarboxylic acid (0.26 g, 1.2 mmol) in 6 ml of thionyl chloride was heated under reflux for 4 h. The excess of thionyl chloride was removed by vacuum distillation and 20 mL of pyridine and 5-(2,4-acetoxyphenyl)tetrazole (2.0 g, 4 mmol) was added. The mixture was heated under reflux for more 24 h. After cooling, the solution was poured into ice/water (250 mL) and the precipitate was filtered off and washed with water. The purification was by column chromatography with dichloromethane/ethyl acetate (95:5) as the eluent, resulting in 1.7 g of compound **10a**. Yield 87%. IR (KBr pellet) ν_{max}cm^{-1}: 3447, 2922, 2851, 1606, 1499. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 9.03 (s, 3H, Ar-H), 7.78 (dd, *J* = 2.2, 8.5 Hz, 3H, Ar-H), 7.71 (d, *J* = 2.2 Hz, 3H, Ar-H), 7.02 (d, *J* = 8.5 Hz, 3H, Ar-H), 4.15 (t, *J* = 6.4 Hz, 6H, O-CH$_2$), 4.11 (t, *J* = 6.4 Hz, 12H, O-CH$_2$), 1.88 (m, 12H, -CH$_2$), 1.52 (m, 12H, -CH$_2$), 1.27 (m, 96H, -CH$_2$), 0.89, 0.88 (t, *J* = 7.2, 7.0 Hz, 18H, -CH$_3$). ^{13}C NMR (CDCl$_3$), δ, ppm: 166.0, 162.8, 153.0, 149.7, 127.3, 126.6, 121.2, 115.8, 113.1, 111.8, 69.8, 69.4, 32.2, 30.0, 29.7, 29.5, 29.4, 26.3, 23.0, 14.4. Elemental analysis (Carlo Erba model E-1110): Calcd. for $C_{102}H_{162}N_6O_9$:C 75.79, H 10.10, N 5.20 . Found: C 75.17, H 10.02, N 5.16. Calcd: m/z 1616.240 (M + H)$^+$. Found: MALDI/MS: m/z 1616.525 [(M + H)$^+$, 100%].

1,3,5-Tris(5-(3,4-bis(octan-3-yloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (10b). Yield 40%. IR (KBr pellet) ν_{max}cm^{-1}: 3439, 2958, 2875, 1602, 1497; ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 9.05 (s, 3H, Ar-H), 7.77 (dd, *J* = 2.1, 8.4 Hz, 3H, Ar-H), 7.70 (d, *J* = 2.1 Hz, 3H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 3H, Ar-H), 4.02, 3.97 (d, 12H, O-CH$_2$), 1.83 (m, 6H, -CH$_2$), 1.54 (m, 12H, -CH$_2$), 1.36 (m, 36H, -CH$_2$), 0.99, 0.98, 0.93 (m, 36H, -CH$_3$).^{13}C NMR (CDCl$_3$), δ, ppm: 166.1, 162.8, 153.3, 150.3, 150.1, 127.3, 126.6, 121.0, 115.6, 112.8, 111.4, 71,9, 71.7, 39.9, 39.7, 30.9, 29.4, 29.4, 29.2, 24.2, 23.4, 14.4, 11.6, 11.5. Elemental analysis (Carlo Erba model E-1110): Calcd. for $C_{78}H_{114}N_6O_9$:C 73.20, H, 8.98, N 6.57 . Found: C 73.66, H 9.27, N 6.77. Calcd: m/z 1279.865 (M + H)$^+$. Found: MALDI/MS: m/z 1280.083 [(M + H)$^+$, 100%].

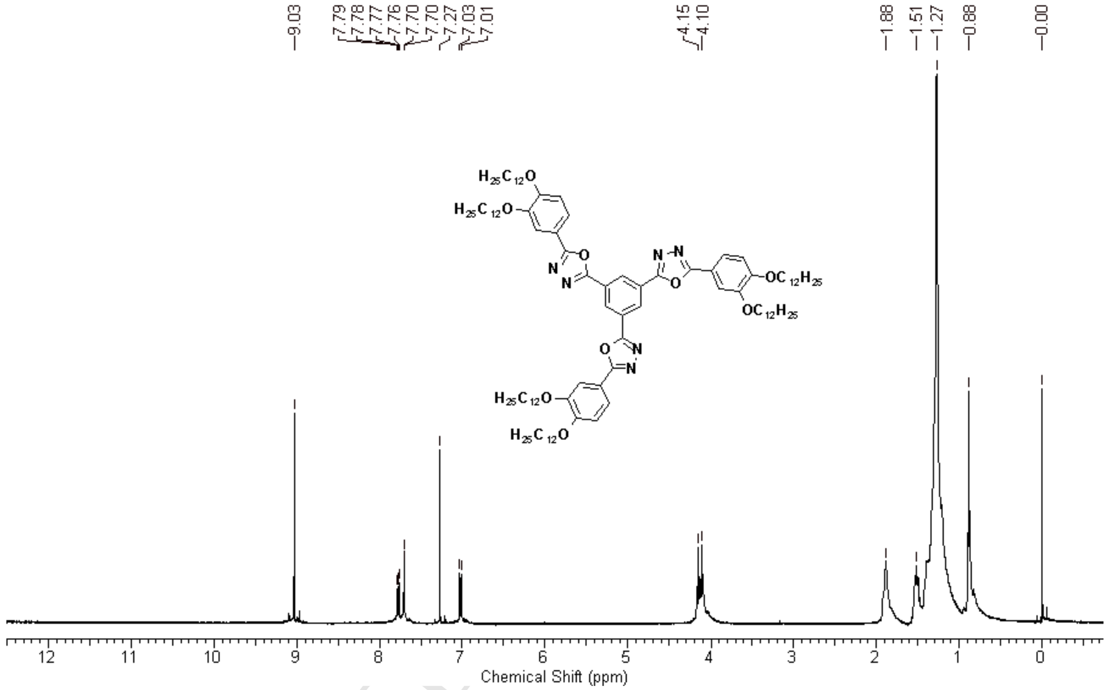
1,3,5-Tris(5-(3,4-bis((*S*)-3-methyloctyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (10c). Yield 39%. IR (KBr pellet) ν_{max}cm^{-1}: 3447, 2963, 2871, 1607. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 9.03 (s, 3H, Ar-H), 7.78 (dd, *J* = 2.0, 8.4 Hz, 3H, Ar-H), 7.71 (d, *J* = 2.0 Hz, 3H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 3H, Ar-H), 5.15(t, 6H, =CH), 4.17, (m, 12H, -OCH$_2$), 2.05 (m, 12H, -CH$_2$), 1.70 (s, 18H, -CH$_3$), 1.62 (s, 18H, -CH$_3$), 1.44 (m, 15H, -CH$_2$), 1.26 (m, 15H, -CH$_2$), 1.02 (m, 18H, -CH$_3$). ^{13}C NMR (CDCl$_3$), δ, ppm: 166.0, 162.8, 153.0, 149.7, 131.6, 131.5, 127.3, 126.6, 125.0, 124.9, 121.2, 115.9, 113.0, 111.8, 68.1, 67.8, 37.6, 37.5, 36.4, 36.2, 30.0, 26.0, 25.8, 20.0, 18.0 . Elemental analysis (Carlo Erba model E-1110): Calcd. for $C_{84}H_{126}N_6O_9$:C 73.97, H, 9.31, N, 6.16. Found: C 73.90, H 9.83, N 6.04. Calcd: m/z 1435.959 (M + H)$^+$. Found: MALDI/MS: m/z 1436.207 [(M + H)$^+$, 100%].

5,5'-(5-(5-(3-(3-(Dodecyloxy)benzyloxy)-4-(4-(dodecyloxy)benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-1,3-phenylene)bis(2-(3,4-bis(4-(dodecyloxy)benzyloxy)phenyl)-1,3,4-oxadiazole) (10d). Yield 53%. IR (KBr pellet) ν_{max}cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 8.89 (s, 3H, Ar-H), 7.75 (d, *J* = 8.4 Hz, 3H, Ar-H), 7.42, 7.36 (d, *J* = 8.2, 8.2 Hz, 12H, Ar-H), 7.07 (d, *J* = 8.4 Hz, 3H, Ar-H), 6.92, 6.90 (d, *J* = 8.2, 8.2 Hz, 12H, Ar-H), 5.20, 5.10 (s, 12H, Ar-CH$_2$), 3.95 (m, 12H, O-CH$_2$), 1.76 (m, 12H, -CH$_2$), 1.40 (m, 12H, -CH), 1.25 (s, 96H, -CH$_2$), 0.87 (mt, 18H, -CH$_3$) .^{13}C NMR (CDCl$_3$), δ, ppm: 165.4, 162.4, 159.1, 152.5, 149.3, 129.2, 129.0, 128.4, 128.2, 126.8, 126.5, 121.5, 116.1, 114.6, 113.1, 71.3, 70.1, 68.0, 31.9, 29.7, 29.6, 29.4, 26.1, 22.7, 14.1. Elemental analysis (Carlo Erba model E-1110): Calcd. for $C_{144}H_{198}N_6O_{15}$: C 76.76, H 8.86, N 3.73. Found: C 76.38, H 8.98, N 3.82. Calcd: m/z 2253.5021 (M + H)$^+$. Found: Q-TOF/MS m/z: 2253.5090 [(M + H)$^+$, 100%].

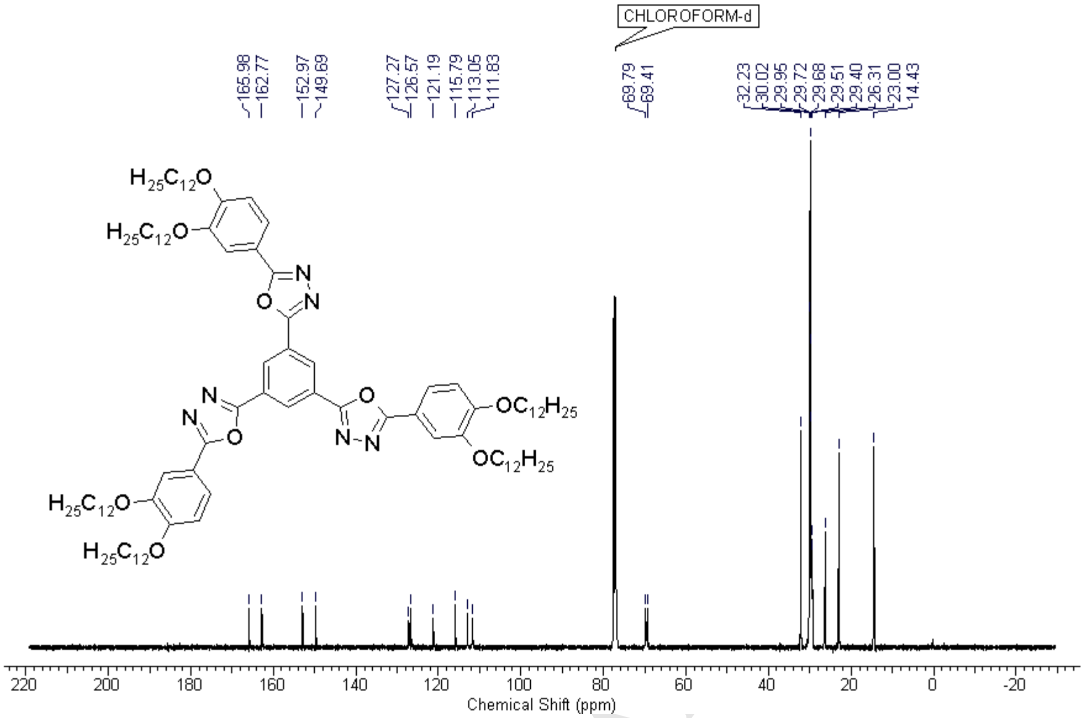
1,3,5-Tris-(5-(3,4-bis(undecyloxy-1-ol)-1,3,4-oxadiazole-2-yl)benzene (10f). 1,3,5-benzenetricarboxylic acid (0.19 g, 0.9 mmol) in 5 ml of thionyl chloride was heated under reflux for 4 h. The excess of thionyl chloride was removed by vacuum distillation and 20 mL of pyridine and compound **8e** (1.7 g, 2.8 mmol) was added. The mixture was heated under reflux for more 24 h. After cooling the room temperature, the solution was poured in ice/water (250 ml) and the precipitate was filtered off and washed with water, obtaining the compound **10f** with acetyl group, it wasn't isolated. Then, immediately the compound **10f** was hydrolyzed using 0.34 g (0.9 mmol) of NaOH in 30 mL of THF, after heating under reflux for 12h. The solution was cooled to room temperature, acidified to pH 4 with HCl aqueous solution (15%) and poured in 200 mL of ice/water, and then the precipitate was filtrated. The purification was by column chromatography with dichloromethane/ethyl acetate (95:10) as the eluent, resulting 0.6 g of compound **10f**, with free hydroxyl group at the end of the alkyl chain. Yield 45%; Mp: 109-111 ^{o}C IR (KBr pellet) ν_{max}cm^{-1}: 3397, 2921, 2850, 1605; ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 9.03 (s, 3H, Ar-H), 7.77 (dd, *J* = 2.0, 8.6 Hz, 3H, Ar-H), 7.70 (d, *J* = 2.0 Hz, 3H, Ar-H), 7.02 (d, *J* = 8.6 Hz, 3H, Ar-H), 4.15, 4.11(t, *J* = 4.3, 4.3 Hz, 12H, -OCH$_2$), 3.65 (m, 12H, HO-CH$_2$-), 1.91 (m, 12H, -CH$_2$), 1.59 (m, 12H, -CH$_2$), 1.32 (s, 84H,-CH$_2$).^{13}C NMR (CDCl$_3$), δ, ppm: 166.2, 153.2, 149.9, 127.5, 124.9, 121.4, 116.0, 113.3 112.1, 111.7, 70.0, 69.6, 63.5, 33.3, 32.4, 30.7, 30.2, 30.1, 30.0, 29.9, 29.7, 29.5, 26.5, 26.2, 23.2, 14.6. Elemental analysis (Carlo Erba model E-1110): Calcd. for $C_{96}H_{150}N_6O_{15}$: C 70.81, H 9.29, N 5.16. Found: C 70.17, H 9.69, N

5.02. MALDI/MS: Calcd: m/z 1650.106 $(M + Na)^+$. Found: MALDI/MS: m/z 1650.525 $[(M + Na)^+$, 100%].

1.0. NMR spectra of compounds **10a-d** and **10f**.

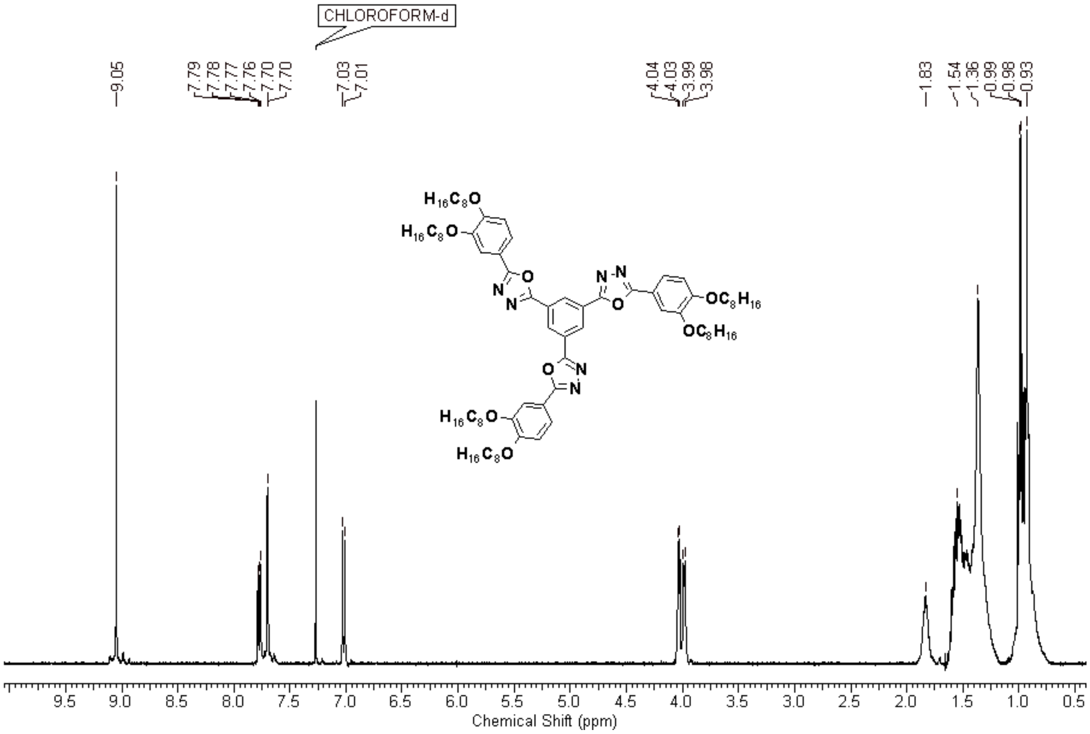


a)

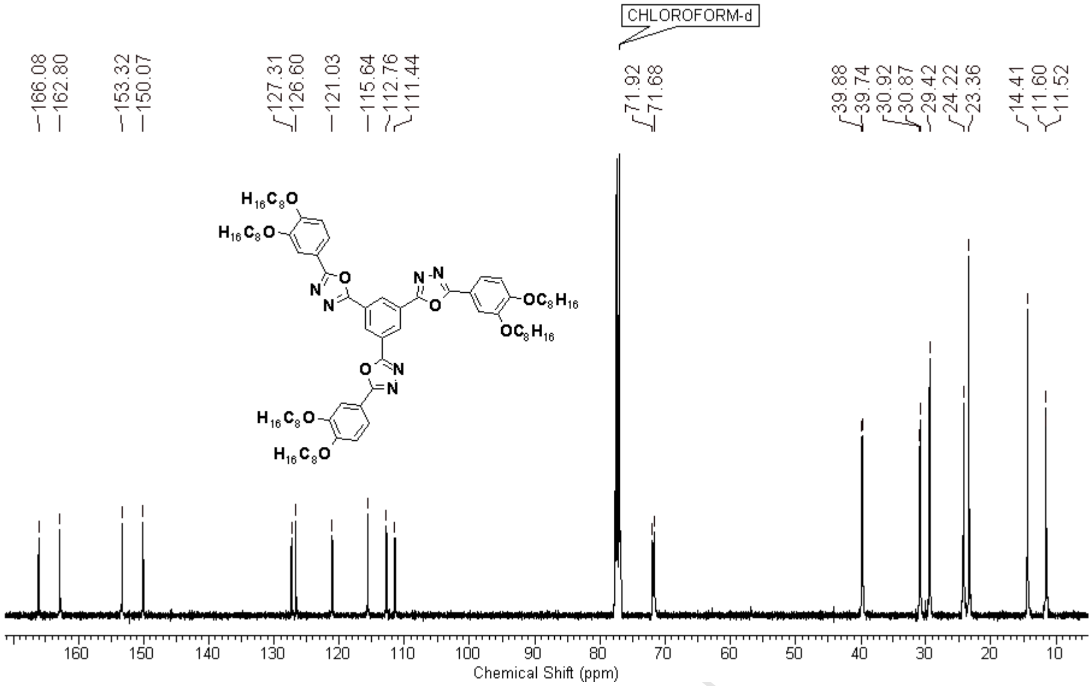


b)

Figure S1. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of compound **10a** (CDCl$_3$).

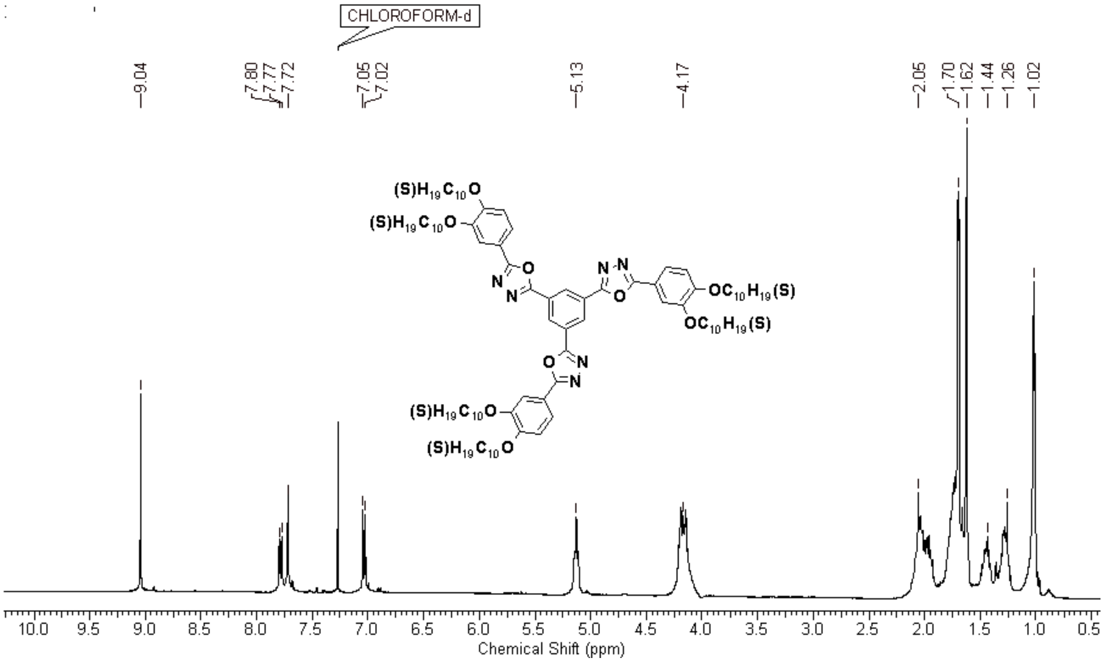


a)

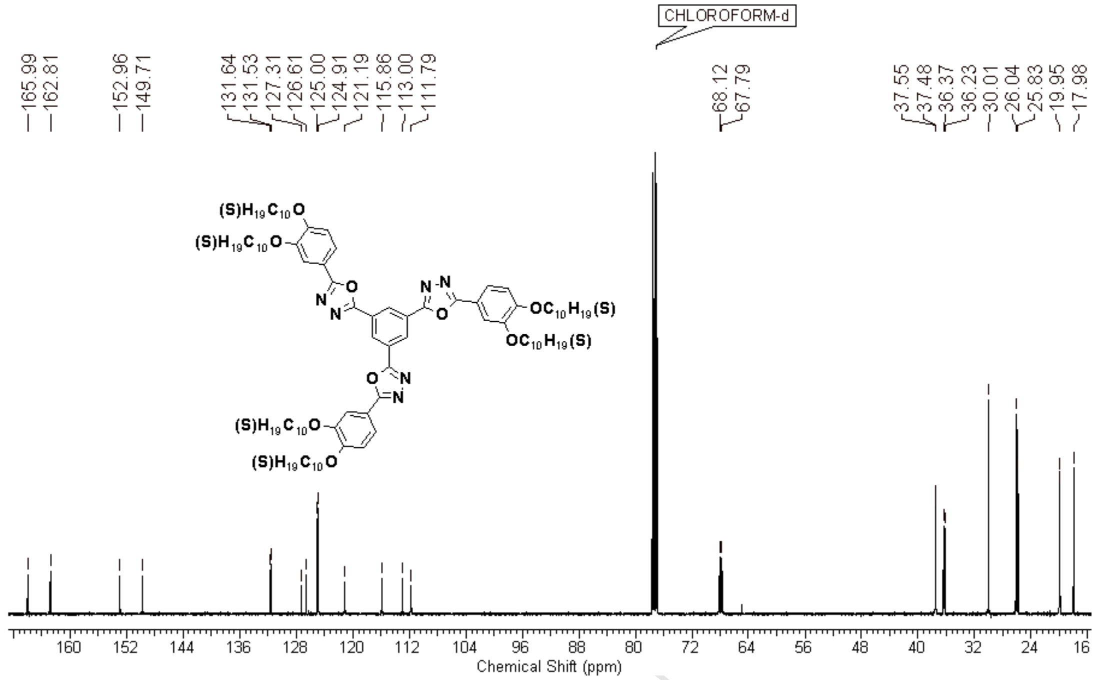


b)

Figure S2. ^{1}H NMR (a) and ^{13}C NMR(b) spectrum of compound **10b** (CDCl$_3$).

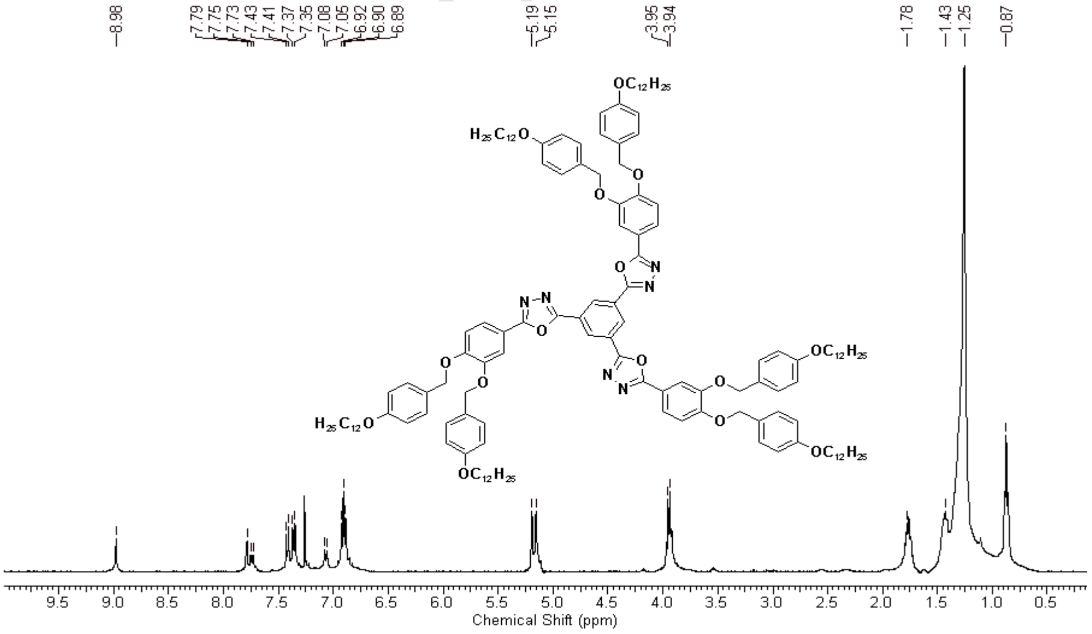


a)

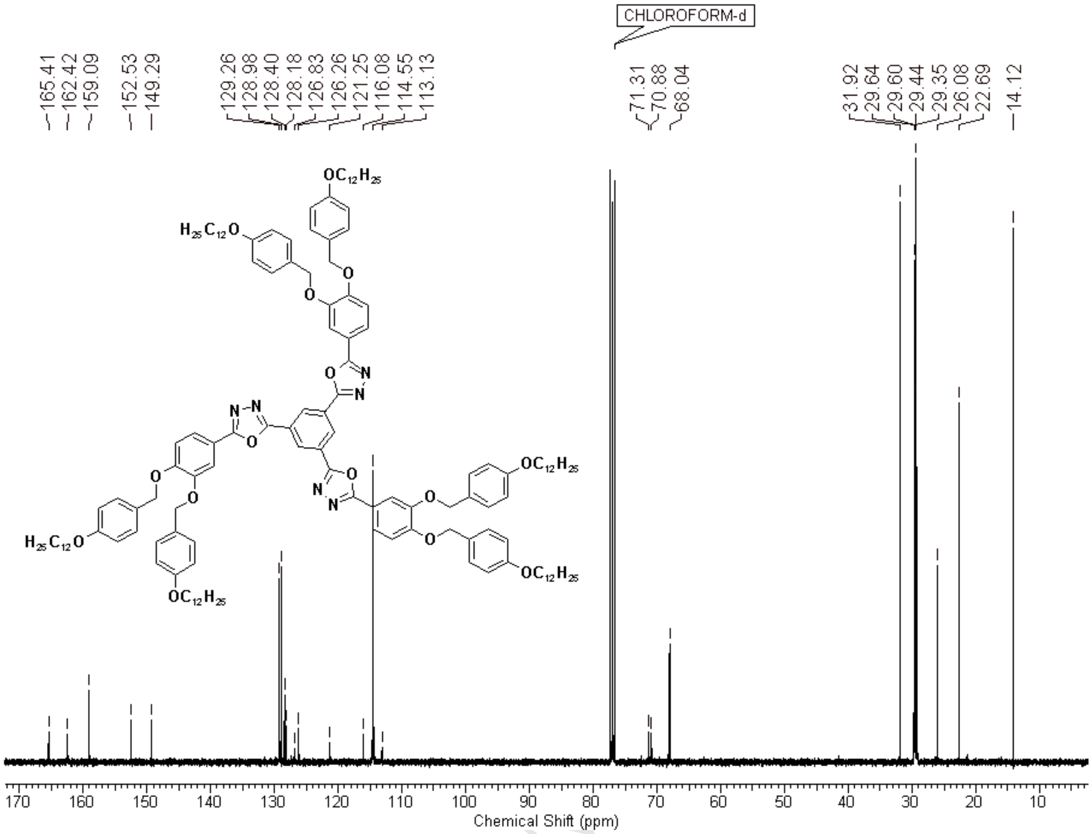


b)

Figure S3. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of compound **10c** ($CDCl_3$).

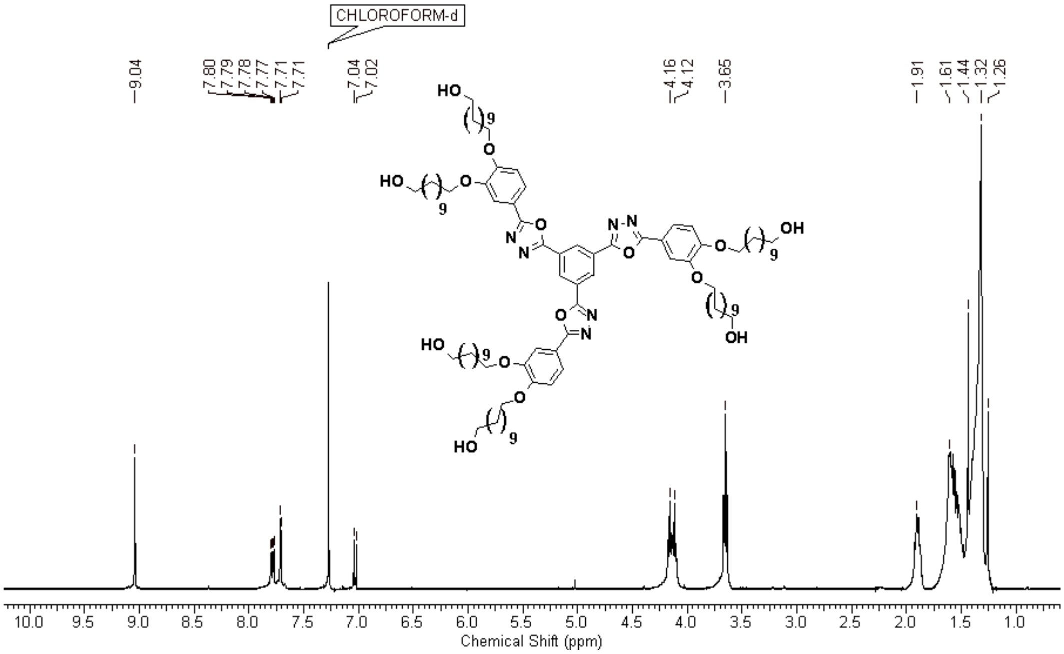


a)

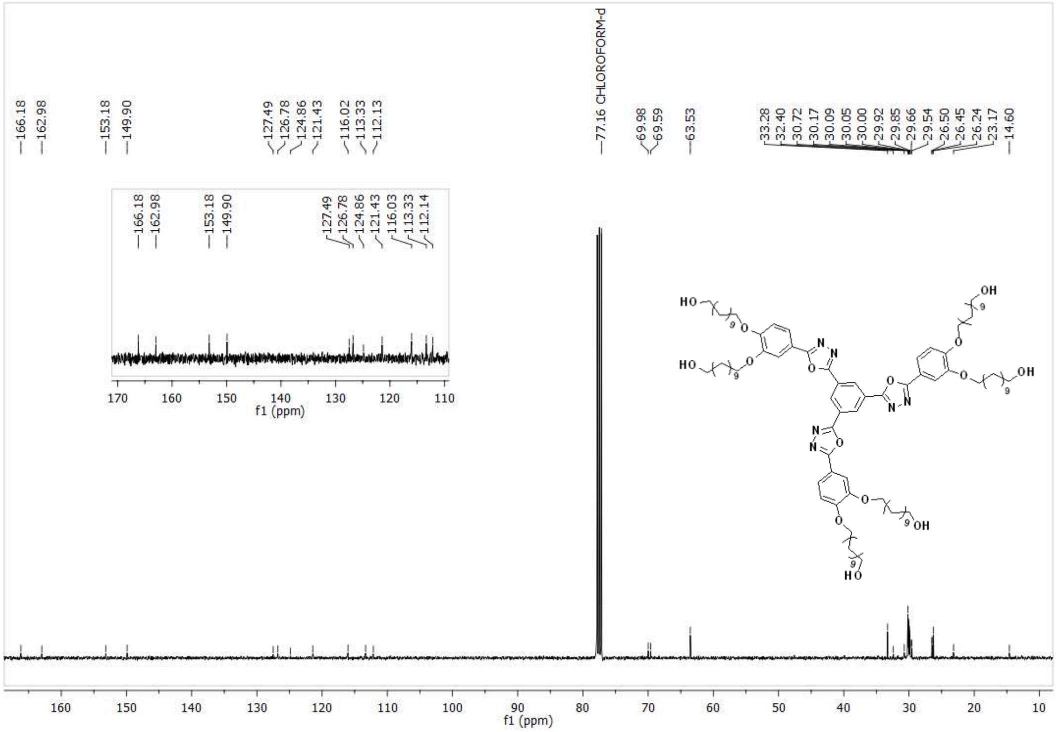


b)

Figure S4. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of compound **10d** (CDCl$_3$).



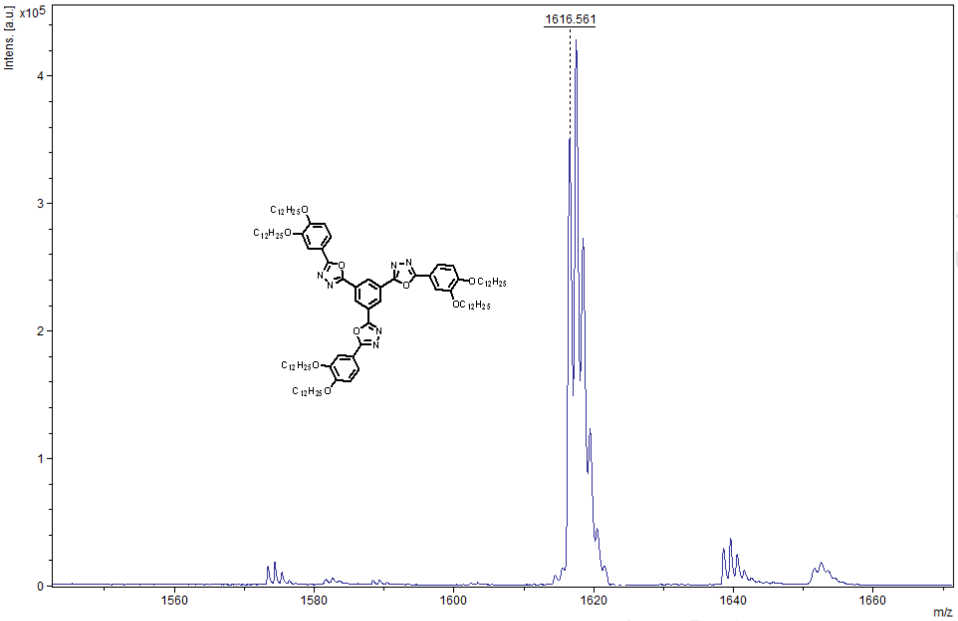
a)



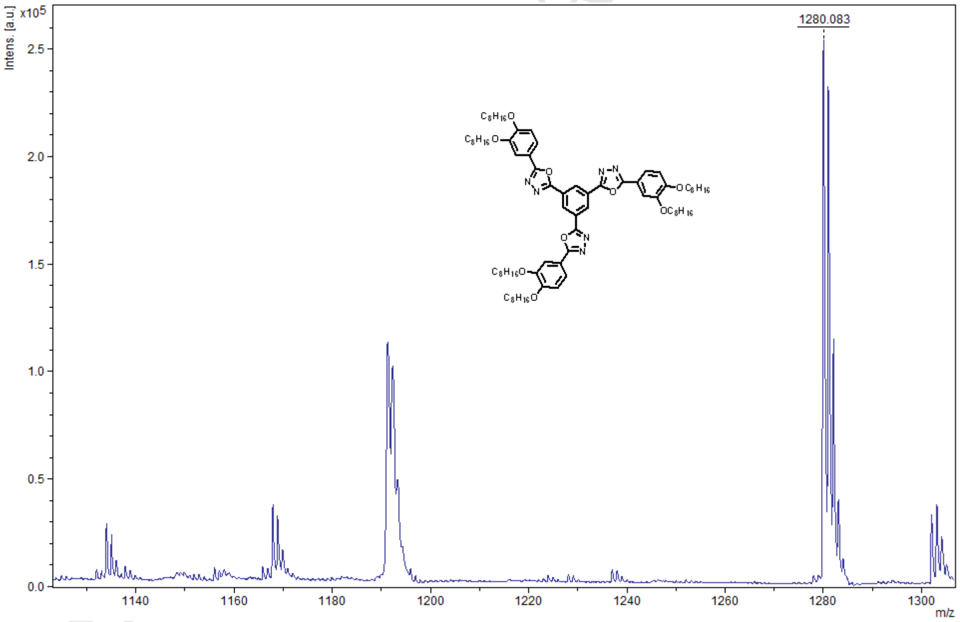
b)

Figure S5. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of compound **10f** ($CDCl_3$).

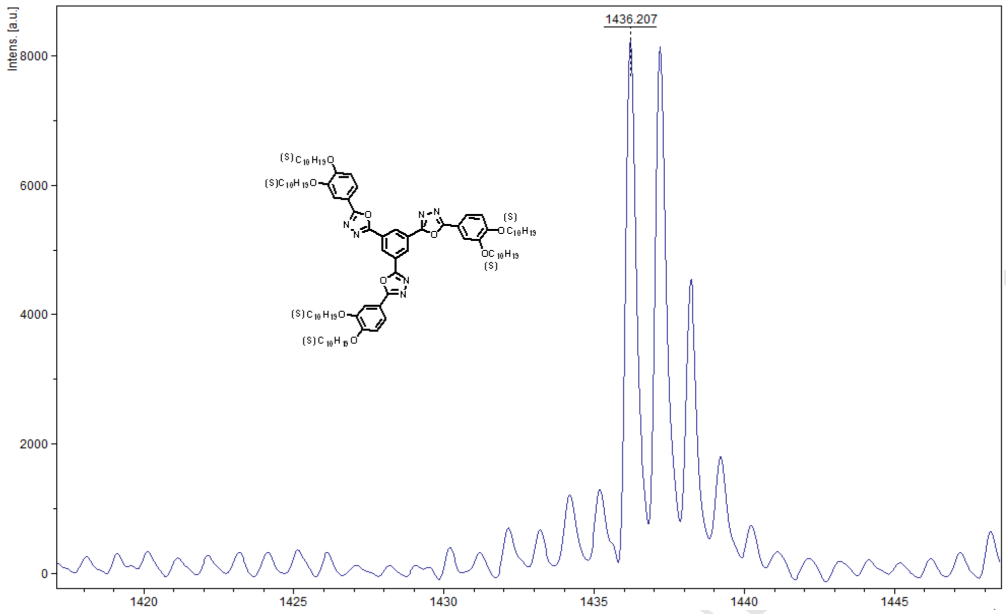
1.1. MS spectra


Intens. [a.u.]
x10^5
4
3
2
1
0
1616.561
1560
1580
1600
1620
1640
1660
m/z
C12H25O
C12H25O
OC12H25
OC12H25
C12H25O
C12H25O
N
O

(**10a**)

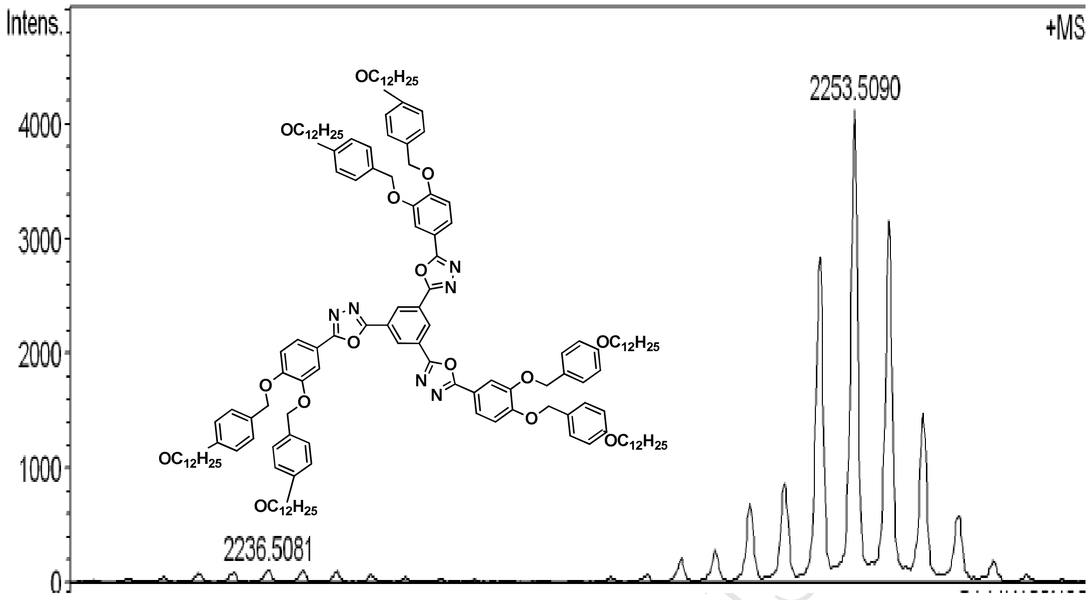

Intens. [a.u.]
x10^5
2.5
2.0
1.5
1.0
0.5
0.0
1280.083
1140
1160
1180
1200
1220
1240
1260
1280
1300
m/z
C8H16O
C8H16O
OC8H16
OC8H16
C8H16O
C8H16O
N
O

(**10b**)

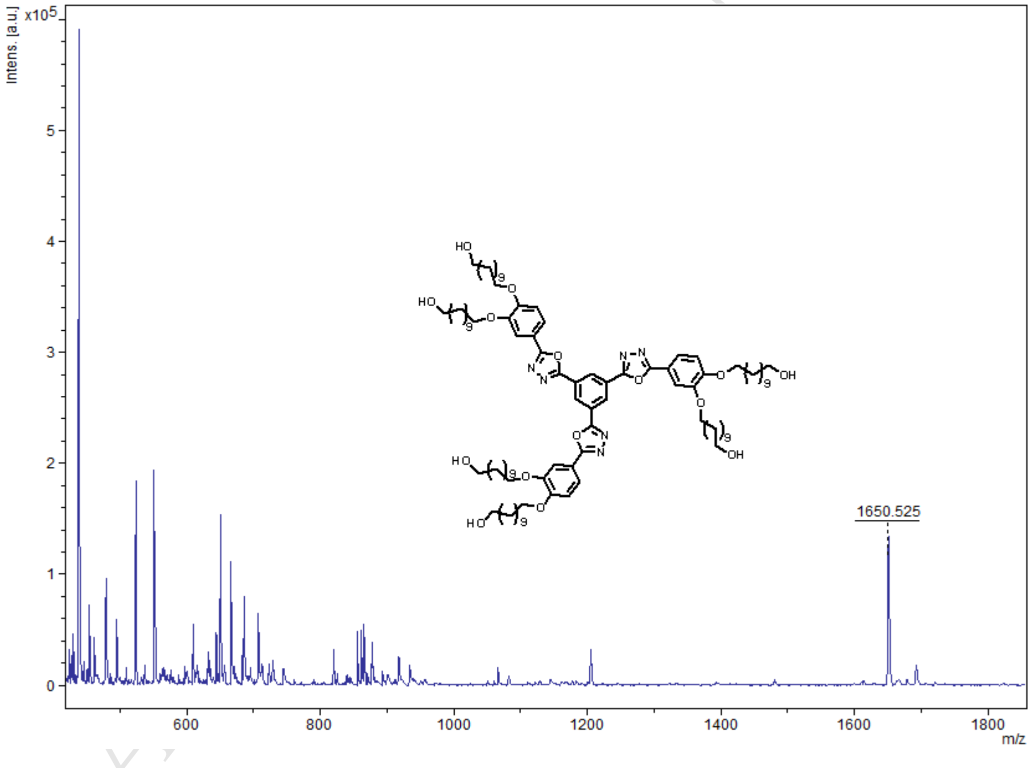


1436.207
Intens. [a.u.]
8000
6000
4000
2000
0
1420
1425
1430
1435
1440
1445
(S)C10H19O
(S)C10H19O
N
N
O
N
N
O
(S)
OC10H19
OC10H19
(S)
O
N
N
(S)C10H19O
(S)C10H19O

(10c)



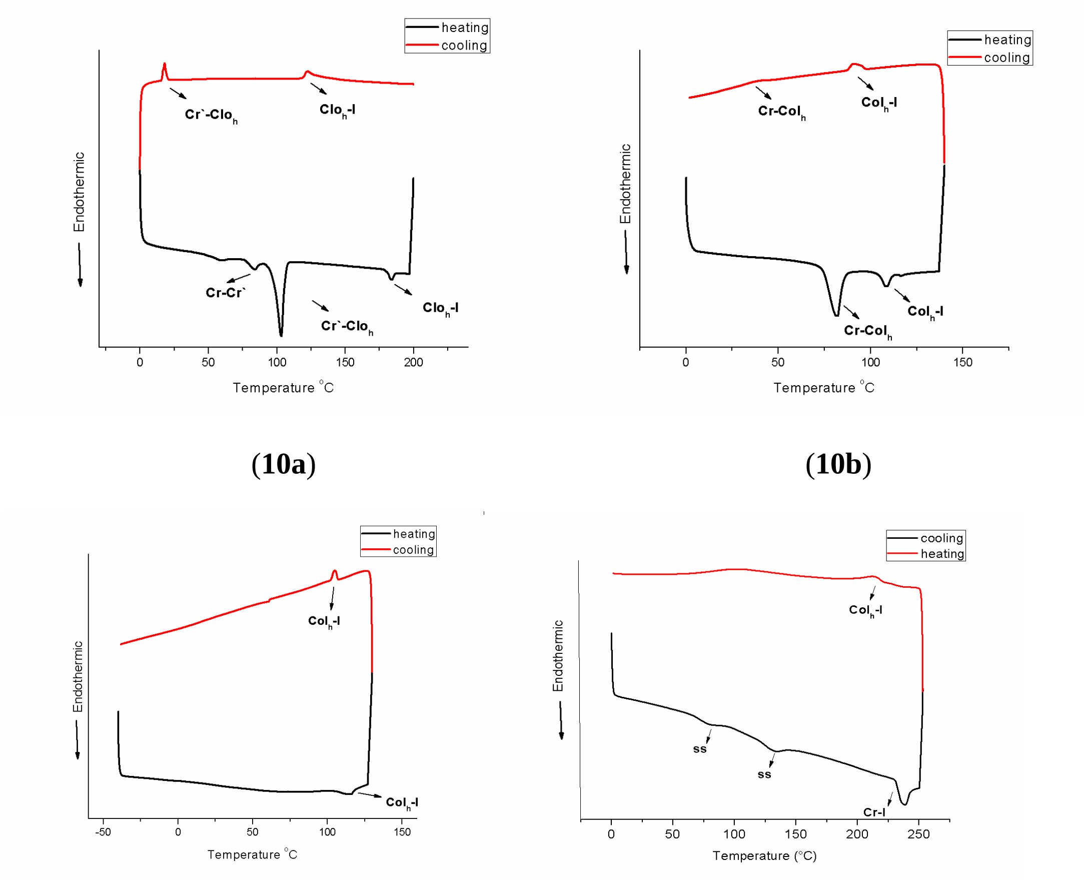
10d



10f

Figure S6. MALDI-MS spectra of compounds **10a-d** and **10f**.

1.2. DSC Thermograms



(10a) (10b)

(10c) (10d)

Figure S7. DSC curves of the final compounds **10a-d**, 10°C/min, first scans.

1.3. X-Ray diffraction (XRD)

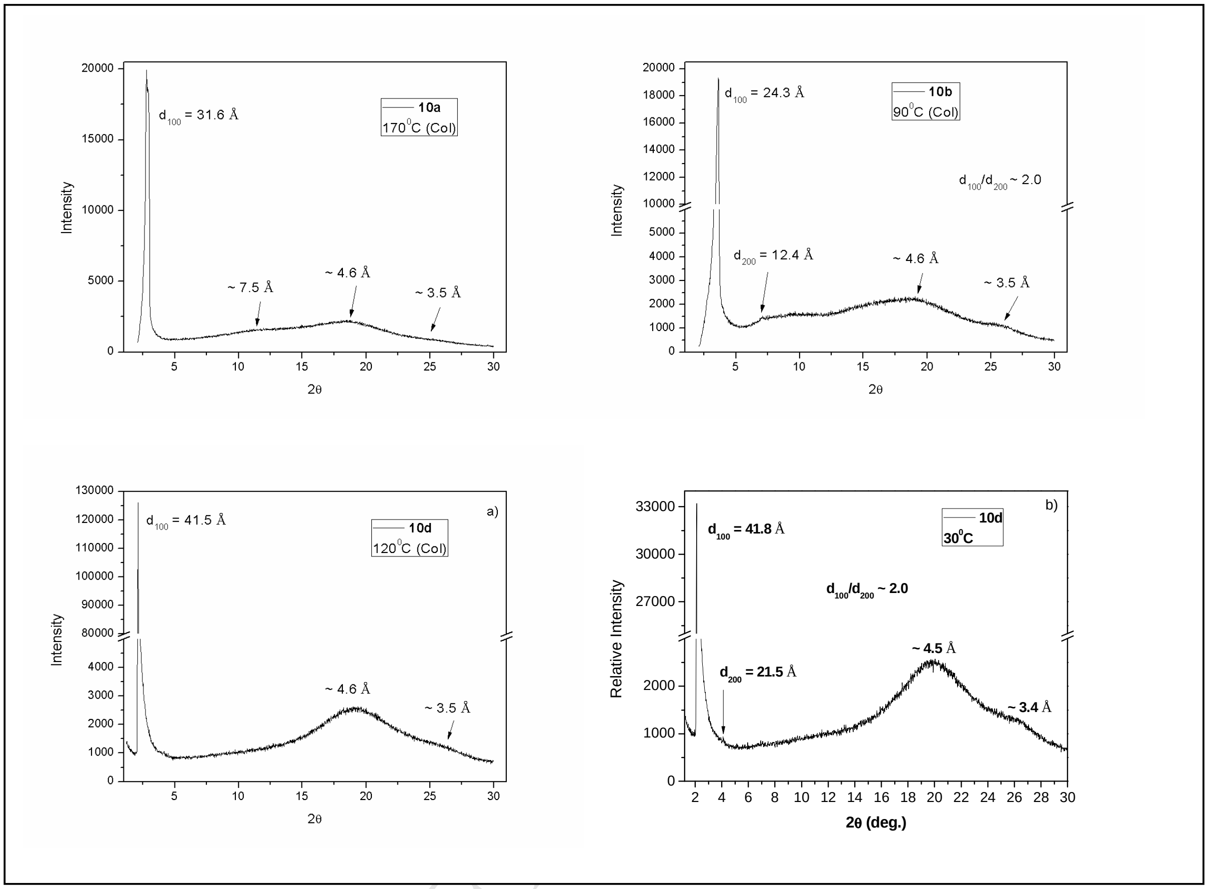
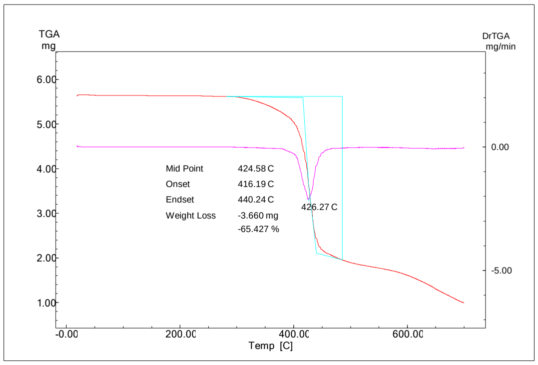


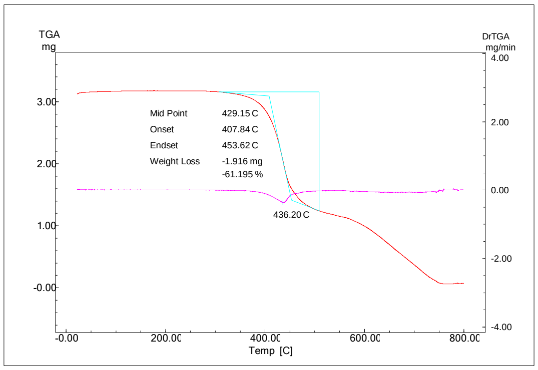
Figure S8. X-ray diffraction patterns of 1,3,4-oxadiazole **10a**, **10b** and **10d** (a, b). Col$_h$ mesophase: the reflections (100), (110), and (200) are due to the long-range intercolumnar ordering.

Table SI. X-ray diffraction data for the mesophases of the compounds **10a-d**.

Compound	Mesophase	Temp.	Parameters	d_{obs}(Å)	d_{calc}(Å)	(*hkl*)
10a	Col_h	150 ^{o}C	**a**= 35.9 Å	31.1	31.1	100
				17.9	18.0	110
			h = 3,4 Å	16.1	15.6	200
10b	Col_h	90 ^{o}C	**a**= 28.0 Å	24.3	24.3	100
			h = 3,4 Å	12.4	12.2	200
10c	Col_h	30 ^{o}C	**a**= 31.2 Å	27	27	100
			h = 3,4 Å	13.8	13.5	200
10d	Col_h	120 ^{o}C	**a**= 47.9 Å	41.5	41.5	100
			h = 3,4 Å			
10d	Col_h	30 ^{o}C	**a =** 48.3Å	41.8	41.8	100
			h = 3,4 Å	21.5	20.9	200

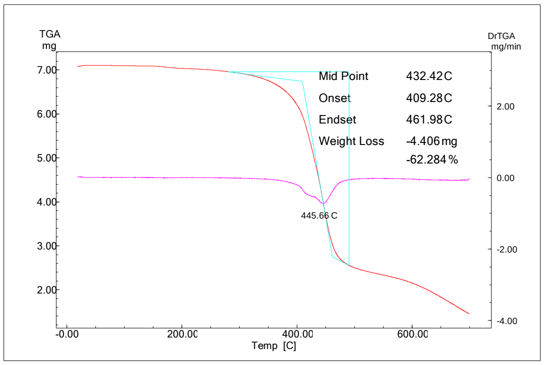
1.4. TGA curves

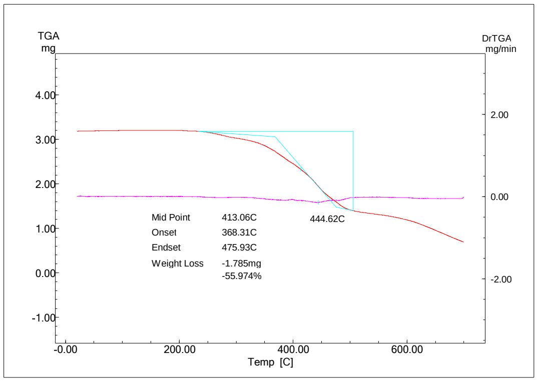




(10a)

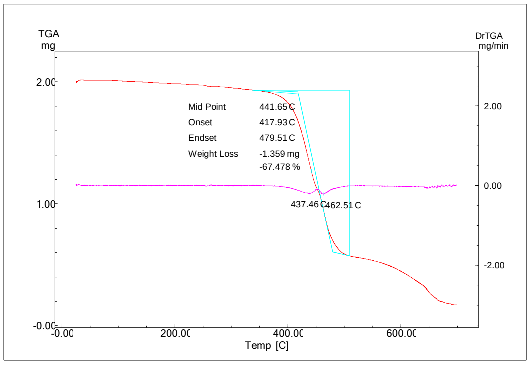
(10b)





(10c)

(10d)



(10f)

Figure S9. TGA curves of the final compounds **10a-d** and **10f**.

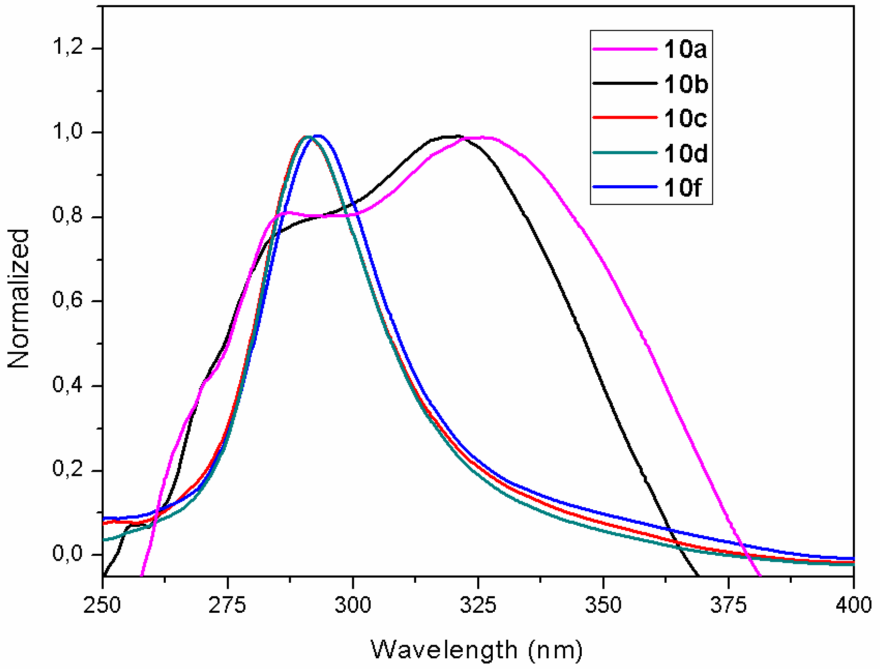
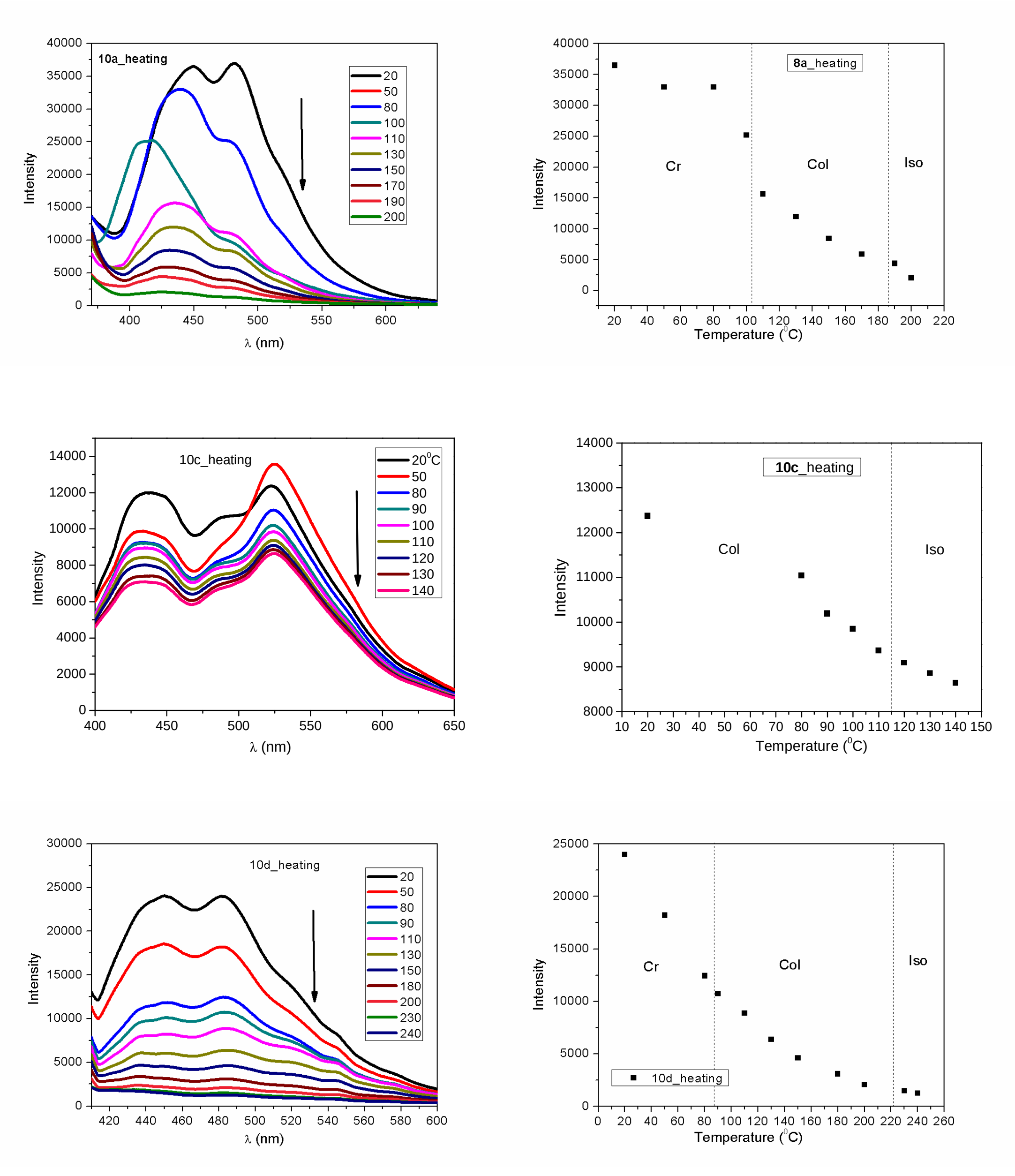


Figure S10. Absorbance of compounds **10a-d** and **10f** in thin solid films at room temperature.



a)

b)

Figure S11. (a) Emission spectra of the compounds **10a**, **10c** and **10d** in solid state. (b) Plot of emission intensity of the maximum wavelength *vs* temperature.

Cyclic Voltammetry. The voltammogram was recorded at scan rate of 25 mV s^{-1} from a **10c** solution (10^{-3} mol.dm^{-3}) in dichloromethane in the presence of 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte.

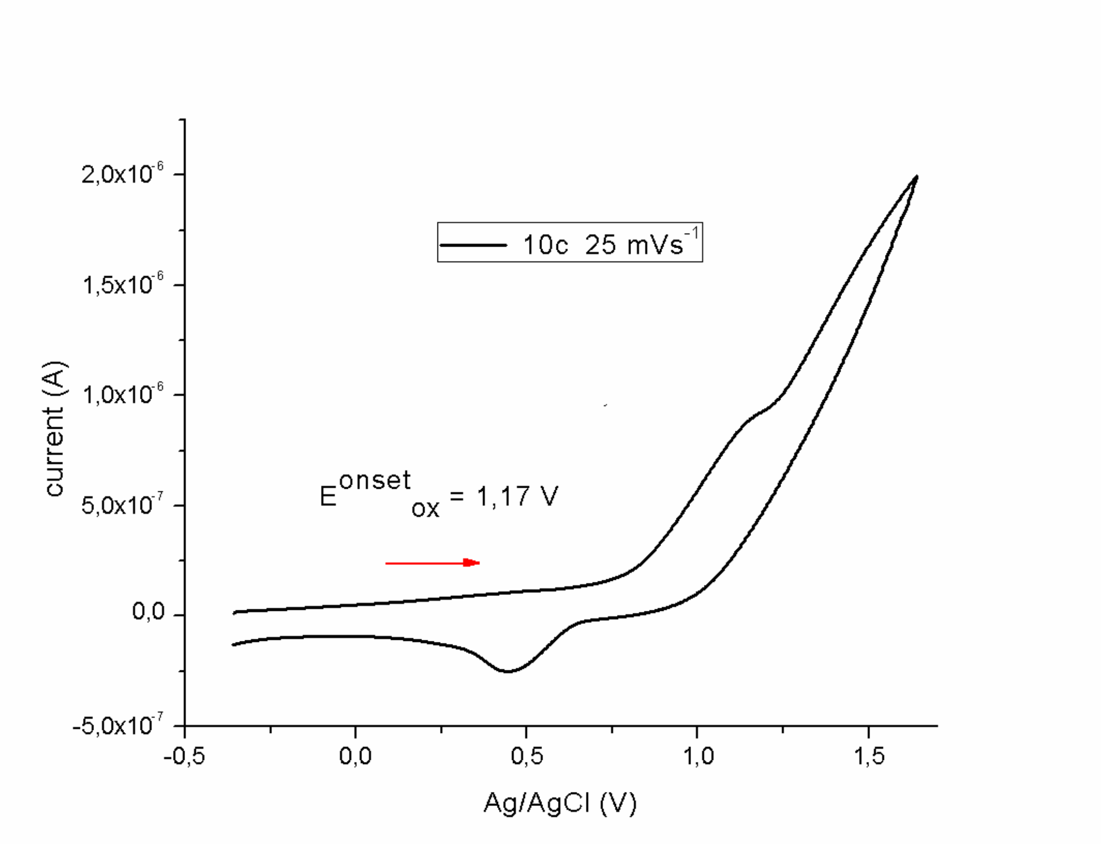


Figure S12: Voltammogram of compound **10c**. Scan rate 25 mV/ s^{-1}.

The onset potential oxidation was determined at 1.17 V. The E_{HOMO} value was calculated using the relationship:

E_{HOMO} = -4.8 – (1.17 – 0.76) ~ -5.21 eV and E_{HOMO} (ferrocene) = -4.8 eV.

Table: Cyclic Voltammetry data for the compound **10c.**

Compound	**E_{ox}[a] (vs. Fc/Fc$^+$)**	**E_{HOMO}[d] (eV vs.vacuum)**	**E_{LUMO}[b] (eV vs.vacuum)**	**E_g[c] (eV)**

10c	1.51	-5.21	-1.41	3.80

[a] E_{ox} (vs. Fc/Fc+) = E_{ox} (vs. Ag^+) – 0.76

[b] $E_{HOMO} = (-4.8 - E_{ox})$[1]

[c] Determined from absorption spectrum of the film [2]

[d] $E_g = E_{HOMO} - E_{LUMO}$

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