Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Cristiano, Rodrigo , Santos, Deise Maria Pereira de Oliveira and Gallardo, Hugo(2005) 'Synthesis and characterization of low molecular mass luminescent liquid crystalline materials with 1,3,4-oxadiazole units', Liquid Crystals, 32: 1, 7 — 14
To link to this Article: DOI: 10.1080/02678290412331329288
URL: http://dx.doi.org/10.1080/02678290412331329288

Liquid Crystals, Vol. 32, No. 1, January 2005, 7–14

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Synthesis and characterization of low molecular mass luminescent liquid crystalline materials with 1,3,4-oxadiazole units

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(*Received 1 July 2004; accepted 21 September 2004*)

The synthesis, and liquid crystalline and photophysical properties of luminescent liquid crystalline compounds based on 1,3-bis[5-(4-alkoxyphenyl)-1,3,4-oxadiazole-2-yl]benzene (two-fold symmetry) **I** and 1,3,5-tris[5-(4-alkoxyphenyl)-1,3,4-oxadiazole-2-yl]benzene **II** (three-fold symmetry) are described. The mesophases were characterized using polarizing optical microscopy and differential scanning calorimetry. In addition, all compounds showed blue fluorescence with emission maxima between 366 and 382 nm, and good quantum yields of photoluminescence (Φ_{PL}=45%).

1. Introduction

Recent extensive studies have shown that organic materials exhibit a variety of interesting optical, electrical, photoelectric, and magnetic properties in the solid state [1, 2]. A wide range of materials has been reported for use in electroluminescence (EL) devices; these vary from low molecular mass materials to processable polymers [3]. The design and fabrication of efficient light emitting devices (LEDs) based on organic materials is an area of active research due to their possible applications in large area display technology [4, 5]. One of the most fascinating advantages in using these organic materials is the wide selection of emission colours in EL displays attainable through the molecular design of organic materials. Liquid crystals are one of the few classes of organic materials to have entered the field of sophisticated electronic applications, principally as displays [6, 7]. Discotic liquid crystalline materials have been proposed for some time as potential candidates for the active layer in organic-based optoelectronic devices such as LEDs, photovoltaic cells (PVCs), and field-effect transistors (FETs) [8, 9]. Much effort has been devoted in recent years to the development of new organic materials and appropriate device structures to obtain high efficiency and stable devices with defined emission colours.

In this context, our interest has been focused on low molecular mass organic compounds containing two or more 1,3,4-oxadiazole units. 1,3,4-oxadiazole derivatives are accessible by several preparative methods and are known for their high thermal and hydrolytic stability and resistance to oxidative degradation; they usually exhibit a high photoluminescence quantum yield [10]. The electron-accepting property of the oxadiazole ring renders substances containing an oxadiazole group useable as electron-transport layers in organic LEDs. In this paper, we report the synthesis of new compounds, 1,3,4-oxadiazole derivatives **I** and **II**, with two- and three-fold symmetry, and their photophysical and thermal properties (figure 1). They were characterized by ^{1}H and ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and UV-visible and fluorescence spectroscopy. Specific properties of interest are (i) changes in thermal transitions and liquid crystalline behaviour, (ii) the following optical properties: absorption and emission spectra in solution, Stokes shifts, emission quantum yield and lifetimes of the excited states.

2. Experimental

2.1. *Materials and methods*

All reagents used in the synthesis were purchased from Aldrich Chemical Company (USA); solvents were used as received from E. Merck. Elemental analyses were performed using a Perkin-Elmer model 2400 instrument. Infrared spectra were recorded on a Perkin-Elmer model 781 spectrometer in KBr disk or film. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC-200F spectrometer operating at 200 and 50.4 MHz, respectively. Chemical shifts are reported relative to tetramethylsilane in units of ppm.

Optical textures and transition temperatures for the compounds were observed under a polarizing

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331329288

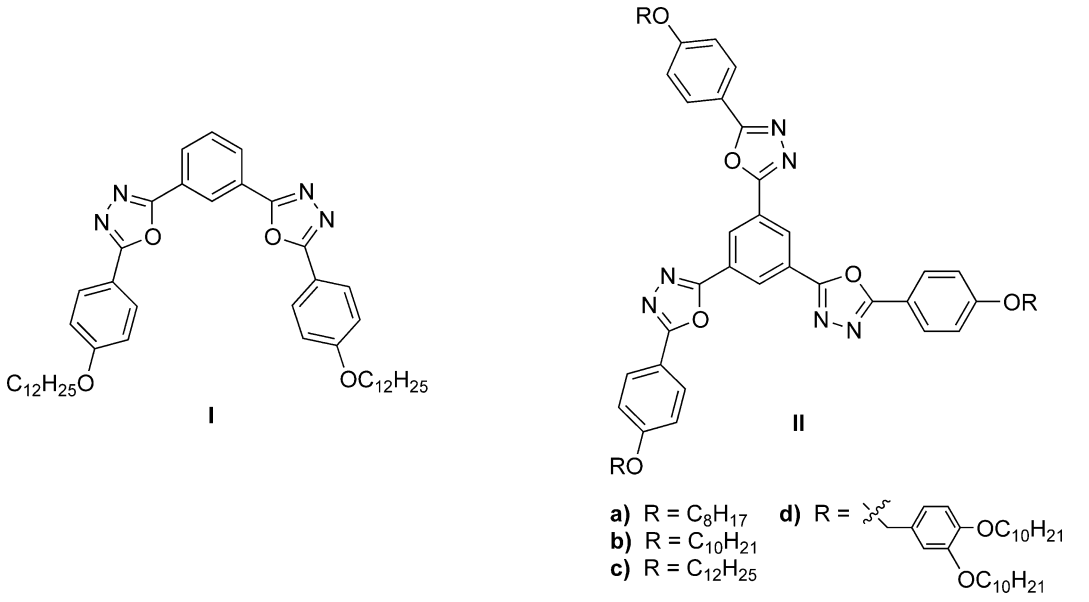


Figure 1. Structures of 1,3,4-okadiazole derivatives **I** and **II**.

microscope (Olympus BX-50) equipped with a Mettler FP 82 hot-stage. Absorption spectra were obtained with a Hitachi model UV 3000 spectrophotometer using spectroscopic grade solvent in a 1 cm optical path length quartz cell. Fluorescence studies were conducted with a Hitachi model F-4500 fluorescence spectrophotometer with excitation wavelength at the absorption maxima. Fluorescence quantum yields were estimated by comparison of standard 1.0M quinine sulphate in H_2SO_4 (Φquinine=0.546). The luminescence decays of the compounds were measured by the single photon counting technique using a CD-900 Edinburgh spectrometer operating with a hydrogen-filled nanosecond flash lamp at 40 kHz pulse frequency.

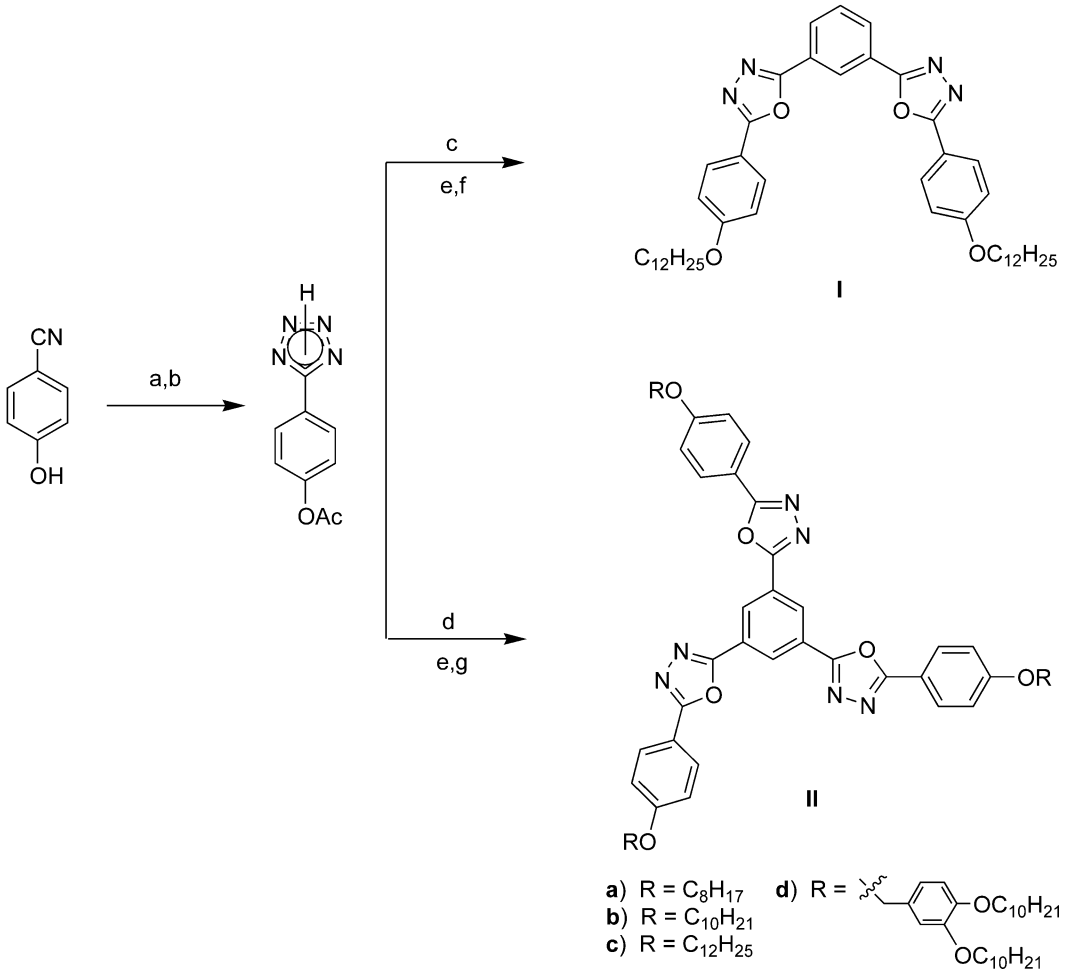
2.2. *Synthesis*

The synthetic route to compounds **I** and **II** involved a tetrazole intermediate, and is outlined in the scheme.

2.2.1. 5-(4-Hydroxyphenyl)tetrazole [11]. A suspension of 0.15 mol of 4-hydroxybenzonitrile, 37.5 g (0.60 mol) of sodium azide, and 30.9 g (0.60 mol) of ammonium chloride in 100 ml of dimethylformamide (DMF) was stirred overnight at 160°C. After cooling, the mixture was poured into water/ice (250 ml) and acidified with hydrochloric acid. The white precipitate was isolated by filtration and washed with water. Recrystallization from water gave a white solid; yield 80.0% (19.4 g), m.p. 241.8°C. IR (KBr, cm^{-1}) ν_{max}: 3420, 2710–2630 (broad), 1614, 1414, 1280, 840. ^1H NMR (200 MHz, DMSO-d_6) δ=10.30 (br s, 1H, OH), 7.95 (d, J=8.4 Hz, 2H, C_6H_4), 7.05 (d, J=8.4 Hz, 2H, C_6H_4), 4.65 (br s, 1H, CN_4H). Elemental analysis: $C_7H_6N_4O$ requires C 54.13, H 5.12, N 31.33; found C 54.28, H 5.16, N 31.68%.

2.2.2. 5-(4-Acetoxyphenyl)tetrazole. To a suspension of 5-(4-hydroxyphenyl)tetrazole (50 mmol) in 30 ml of water, a solution of 3 M sodium hydroxide was added until the solid was completely dissolved. Ice and acetic anhydride (5 ml, 53 mmol) were then added and the mixture vigorously stirred for 10 to 15 min. The reaction mixture was acidified with hydrochloric acid. The acetate was isolated by filtration, washed with cold water and recrystallized from ethanol/water to give white crystals, yield 10 g (98.0%), m.p. 182°C. IR (KBr, cm^{-1}) ν_{max}: 2716–2620 (broad), 1754, 1614, 1502, 1212, 912. ^1H NMR (200 MHz, DMSO-d_6) δ=8.18 (d, J=8.7 Hz, 2H, C_6H_4), 7.49 (d, J=8.7 Hz, 2H, C_6H_4), 6.21 (Br s, 1H, CN_4H), 2.39 (s, 3H, $CH_3CO_2^-$). Elemental analysis: $C_9H_8N_4O_2$ requires C 54.79, H 5.06, N 25.46; found C 54.82, H 5.10, N 25.59%.

2.2.3. 1,3-Bis[5-(4-acetoxyphenyl)-1,3,4-oxadiazole-2-yl]benzene. Isophthalic acid (1.03 g, 6.2 mmol) in 10 ml of thionyl chloride was heated under reflux for 4 h. The excess of thionyl chloride was removed by vacuum distillation, and to the residue 5 ml of pyridine was added; 5-(4-acetoxyphenyl)tetrazole (2.53 g, 12.4 mmol) dissolved in 10 ml of pyridine was then added dropwise. The mixture was heated under reflux until the evolution of N_2 ceased (about 2 h.). After cooling, the solution was poured into ice/water (250 ml) and the precipitate was filtered off and washed with water and hot ethanol



Scheme. Conditions: a) NaN_3, NH_4Cl, DMF, 160°C 12 h 80%; b) Ac_2O, NaOH/H_2O, 0°C 15 min 98%; c) isophthaloyl dichloride, pyridine, reflux 2 h (83%); d) 1,3,5 benzoyl trichloride, pyridine, reflux 4 h (82%); e) NaOH, H_2O, THF/MeOH, reflux 3 h; f) $C_{12}H_{25}Br$, K_2CO_3, DMF,[KI] (77%); g) $C_nH_{2n+1}Br$, K_2CO_3, DMF, [18-crown-6] (70–74%) or 4-bromomethyl-1,2-didecyloxybenzene, K_2CO_3, DMF, [18-crown-6] (66%).

to give 2.4 g (83% yield) as a white powder, m.p. 245–250°C. IR (KBr, cm^{-1}) ν_{max}: 1759, 1607, 1554, 1193. ^1H NMR (200 MHz, $CDCl_3$) δ=8.86 (s, 1 H, Ar), 8.34 (d, 2 H, J=7.8 Hz, Ar), 8.22 (d, 4 H, J=8.52 Hz), 7.74 (t, 1 H, Ar), 7.32 (d, 4 H, J=8.54 Hz, Ar), 2.36 (s, 6 H, CH_3COO). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=169.55, 165.12, 164.36, 154.21, 130.79, 130.54, 129.20, 125.71, 123.27, 121.91, 21.85. Elemental analysis: $C_{26}H_{18}N_4O_2$ requires C 64.73, H 3.76, N 11.61; found C 64.61, H 3.71, N 11.36%.

2.2.4. 1,3,5-Tris[5-(4-acetoxyphenyl)-1,3,4-oxadiazole-2-yl]benzene. The procedure of § 2.2.3 was followed using 1,3,5-benzenetricarboxylic acid (2 g, 7.53 mmol) and 5-(4-acetoxyphenyl)tetrazole (4.61 g, 22.6 mmol). Purification was performed by boiling the precipitate in ethanol, followed by hot filtration to afford 4.23 g (82% yield) of a white powder, m.p. 301°C. IR (KBr, cm^{-1}) ν_{max}: 2999, 1757, 1607, 1491, 1195. ^1H NMR (200 MHz, $CDCl_3$) δ=9.04 (s, 3 H, Ar), 8.26 (d, 6 H, J=8.6 Hz, Ar), 7.35 (d, 6 H, J=8.6 Hz, Ar), 2.37 (s, 9 H, CH_3COO–). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=169.5, 165.5, 163.4, 154.3, 129.3, 127.9, 126.9, 123.3, 121.5, 21.8. Elemental analysis: $C_{36}H_{24}N_6O_9$ requires C 63.16, H 3.53, N 12.28; found C 62.71, H 3.63, N 12.04%.

2.2.5. 1,3-Bis[5-(4-hydroxyphenyl)-1,3,4-oxadiazole-2-yl]benzene. 1,3-Bis[5-(4-acetoxy phenyl)-1,3,4-oxadiazole-2-yl]benzene (1 g, 2.07 mmol) was suspended in tetrahydrofuran (THF) (50 ml) and methanol (20 ml); sodium hydroxide (0.25 g, 6.21 mmol) dissolved in 5 ml of water was added. After heating under reflux for 1.5 h the reaction mixture was cooled and acidified with concentrated hydrochloric acid. The solvents were evaporated and 200 ml of water added to the crude product and the mixture stirred at room temperature

for 1 h. The white precipitate was filtered off, washed with water, and dried; yield 0.67 g (81%), m.p. >300°C. IR (KBr, cm^{-1}) ν_{max}: 3071, 1594, 1500, 1444. ^1H NMR (200 MHz, DMSO-d_6) δ=10.37 (s, 2 H, OH), 8.65 (s, 1 H, Ar), 8.29 (d, 2 H, J=7.8 Hz, Ar), 8.00 (d, 4 H, J=8.0 Hz, Ar), 7.84 (t, 1 H, J=7.8 Hz, Ar), 6.99 (d, 4 H, J=8.0 Hz, Ar). Elemental analysis: $C_{22}H_{14}N_4O_4$ requires C 66.33, H 3.54, N 14.06; found C 66.09, H 3.62, N, 13.87%.

2.2.6. 1,3,5-Tris-[5-(4-hydroxyphenyl)-1,3,4-oxadiazole-2-yl]benzene. The procedure of §2.2.5 was followed, using 1,3,5-tris[5-(4-acetoxyphenyl)-1,3,4-oxadiazole-2-yl]-benzene (2 g, 2.92 mmol) and 1 g (25 mmol) of sodium hydroxide with 3 h of reflux. The yield was 1.36 g (84%) of a white powder. IR (KBr, cm^{-1}) ν_{max}: 3136, 1609, 1557, 1492, 1247. ^1H NMR (200 MHz, DMSO-d_6) δ=10.54 (s, 3 H, O–H), 8.64 (s, 3 H, Ar), 7.96 (d, 6 H, J=8.3 Hz), 6.98 (d, 6 H, J=8.3 Hz). Elemental analysis: $C_{30}H_{18}N_6O_6$. $2H_2O$ requires C 60.61, H 3.73, N 14.14; found C 61.53, H 3.73, N 13.78%.

2.2.7. 1,3-Bis[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]benzene (I). 0.398 g (1 mmol) of 1,3-bis[5-(4-hydroxyphenyl)-1,3,4-oxadiazole-2-yl]benzene, 0.83 g (6 mmol) of potassium carbonate and a catalytic amount of potassium iodide were suspended in 30 ml of DMF and the mixture held at 100°C for 45 min. 1-Bromododecane (0.5 ml, 2.1 mmol) was added dropwise and the reaction mixture kept at 100°C for a further 20 h. The mixture was cooled to room temperature and filtered, washing with dichloromethane (100 ml). The solution was washed successively with aqueous sodium hydroxide (5%, 2 × 50 ml), brine (2 × 30 ml) and water (2 × 30 ml). The organic phase was dried (Na_2SO_4), filtered and concentrated under vacuum to give 565 mg of the product as a white fluffy solid (77% yield), m.p. 142.8°C. IR (KBr, cm^{-1}) ν_{max}: 2919, 2850, 1610, 1494, 1467, 1255, 831. ^1H NMR (200 MHz, $CDCl_3$) δ=8.83 (s, 1 H, Ar), 8.31 (dd, 2 H, J=7.8 and 1.4 Hz, Ar), 8.10 (d, 4 H, J=8.8 Hz, Ar), 7.71 (t, 1 H, J=7.8 Hz, Ar), 7.04 (d, 4 H, J=8.8 Hz, Ar), 4.05 (t, 4 H, $OC\underline{H}_2$), 1.8 (m, 4 H, $OCH_2C\underline{H}_2$), 1.27 (s, 36 H, CH_2), 0.88 (t, 6 H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=165.7, 163.8, 162.8, 130.6, 130.1, 129.5, 125.8, 125.4, 116.4, 115.7, 68.9, 32.6, 30.3, 30.0, 29.8, 26.7, 23.3, 14.8. Elemental analysis: $C_{46}H_{62}N_4O_4$ requires C 75.17, H 8.50, N 7.62; found C 75.08, H 8.18, N 7.88%.

2.2.8. General procedure for compounds (II) (a, b, c, d). 0.5 g (0.9 mmol) of 1,3,5-tris[5-(4-hydroxyphenyl)-1,3,4-oxadiazole-2-yl]benzene, 1.12 g (8.1 mmol) of potassium carbonate and a catalytic amount of 18-crown-6-ether in 35 ml of DMF were held at 60°C for 30 min. The respective 1-bromoalkane (2.79 mmol) in 5 ml of DMF was added slowly and the mixture kept at 100°C for 30 h. After cooling, the mixture was poured into water (100 ml) and extracted with 100 ml of $CHCl_3$. The organic phase was concentrated to afford the product in analytical purity.

2.2.8.1. *1,3,5-Tris[5-(4-octyloxyphenyl)-1,3,4-oxadiazole-2-yl]benzene (**IIa**)*. Yield: 0.570 g (71%) white powder, m.p. 141.1°C. IR (KBr, cm^{-1}) ν_{max}: 2923, 2851, 1610, 1495, 1468, 1256, 1175. ^1H NMR (200 MHz, $CDCl_3$) δ=9.00 (s, 3 H, Ar), 8.15 (d, 6 H, J=8.7 Hz, Ar), 7.07 (d, 6 H, J=8.8 Hz, Ar), 4.06 (t, 6 H, CH_2O), 1.84 (m, 6 H), 1.33 (br s, 30 H, CH_2), 0.90 (br s, 9 H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=166.13, 163.07, 129.70, 127.43, 126.96, 116.18, 115.78, 69.05, 32.49, 30.37, 30.03, 29.92, 26.69, 23.34, 14.78.

2.2.8.2. *1,3,5-Tris-[5-(4-decyloxyphenyl)-1,3,4-oxadiazole-2-yl]benzene (**IIb**)*. Yield: 0.598 g (68%) white powder. Cr_1 106.9 Cr_2 130.4 Cr_3 135.9 I°C. IR (KBr, cm^{-1}) ν_{max}: 2923, 2852, 1611, 1495, 1256, 1174. ^1H NMR (200 MHz, $CDCl_3$) δ=9.00 (s, 3 H, Ar), 8.15 (d, 6 H, J=8.6 Hz, Ar), 7.06 (d, 6 H, J=8.7 Hz, Ar), 4.06 (t, 6 H, CH_2O), 1.84 (m, 6 H), 1.29 (br s, 42 H, CH_2), 0.88 (br s, 9 H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=166.21, 163.10, 129.75, 127.55, 127.03, 116.21, 115.82, 69.07, 32.60, 30.26, 30.03, 30.06, 29.84, 26.70, 23.38, 14.82. Elemental analysis: $C_{60}H_{78}N_6O_6$ requires C 73.59, H 8.03, N 8.58; found C 74.08, H 8.13, N 8.36%.

2.2.8.3. *1,3,5-Tris-[5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole-2-yl]benzene (**IIc**)*. Yield: 0.704 g (74%) white powder. Cr_1 73.3 Cr_2 124.8 I°C. IR (KBr, cm^{-1}) ν_{max}: 2920, 2849, 1610, 1495, 1257, 1174, 834. ^1H NMR (200 MHz, $CDCl_3$) δ=8.95 (s, 3 H, Ar), 8.13 (d, 6 H, J=8.4 Hz, Ar), 7.05 (d, 6 H, J=8.4 Hz, Ar), 4.04 (t, 6 H, $OC\underline{H}_2$), 1.81 (m, 6 H, $OCH_2C\underline{H}_2$), 1.27 (s, 54 H, CH_2), 0.88 (t, 9 H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=166.1, 163.1, 129.7, 127.4, 126.9, 116.1, 115.7, 69.04, 32.60, 30.31, 30.05, 29.82, 26.68, 23.37, 14.79. Elemental analysis: $C_{66}H_{90}N_6O_6$ requires C 74.54, H 8.53, N 7.90; found C 74.35, H 8.63, N 7.54%.

2.2.8.4. *1,3,5-Tris{5-[4-(3,4-decyloxybenzyloxy)-1,3,4-oxadiazole-2-yl]}benzene (**IId**)*. Yield: 820 mg (52%). Chromatographic column of a sample was evaluated (eluants: hexane/ethyl acetate 3/1 and CH_2Cl_2/ethyl acetate 1/1) for a higher purity. Cr_1 86.7 Cr_2 115.0 Col_h 140.1I°C. IR (KBr, cm^{-1}) ν_{max}: 2922, 2851, 1610, 1496, 1252, 1174, 989. ^1H NMR (200 MHz,

$CDCl_3$) δ=9.03 (s, 3 H, Ar), 8.16 (d, 6 H, J=8.4 Hz, Ar), 7.16 (d, 6 H, J=8.5 Hz, Ar), 7.00–6.92 (m, 9 H, Ar), 5.07 (br s, 6 H, CH_2), 4.02 (br s, 12 H, CH_2), 1.83–1.79 (m, 12 H, CH_2), 1.27 (br s, CH_2), 0.88 (br s, 18 H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ=166.12, 163.08, 162.71, 150.00, 129.77, 129.13, 127.55, 126.98, 121.28, 116.55, 116.20, 114.33, 114.23, 71.08, 70.01, 32.61, 30.31, 30.13, 30.06, 26.74, 23.38, 14.82. Elemental analysis: $C_{111}H_{156}N_6O_{12}$ requires C 75.47, H 8.90, N 4.76; found C 75.06, H 9.12, N 4.98%.

3. Results and discussion

3.1. *Synthesis*

The synthetic route to the preparation of oxadiazoles **I** and **II** was performed via a tetrazole intermediate as shown in the scheme. All compounds synthesized were characterized and identified by ^{1}H and ^{13}C NMR and IR spectroscopy and found to be analytically pure by elemental analyses. The synthetic route involves the formation of 5-(4-hydroxyphenyl)tetrazole by the 1,3-cycloaddition reaction of 4-hydroxybenzonitrile with sodium azide in DMF and subsequent hydroxyl group protection with acetic anhydride. The key step is the reaction of the phenyltetrazole with respective acid chlorides, which leads to oxadiazoles via intramolecular ring transformation. The isophthaloyl dichloride and 1,3,5-benzoyl trichloride were prepared from respective carboxylic acids with thionyl chloride and used immediately. The next steps involve the cleavage of the acetyl group and subsequent alkylation with the appropriate alkyl bromide or 3,4-didecyloxybenzyl bromide.

3.2. *Thermal behaviour*

All the compounds were examined by DSC, TGA and phase assignments were made by POM. The transition temperatures and the texture observations are listed in table 1. Compound **I** exhibits no mesogenic behaviour. This is due to a loss of linearity in the molecule by the presence of the oxadiazole ring, for it is unable to make co-linear disubstitution bonding.

The melting points of the corresponding compounds with threefold symmetry **II** (**a**, **b**, **c**), decrease significantly as the length of the alkoxy chains increases. Compounds **IIb** and **IIc** exhibit monotropic mesomorphism. The optical textures observed are consistent with a hexagonal columnar mesophase. Upon cooling, small isotropic liquid bâtonnets appeared. The bâtonnets grow into larger domains when the sample is further cooled. Further lowering of the temperature encourages further growth of the bâtonnets. Coalescence of the anisotropic domains results in the formation of a pseudo-focal-conic texture, typical of the Col_h mesophase, with subsequent crystallization. Compound **IIa** does not exhibit mesogenic behaviour, which indicates that a minimum chain length for all three alkoxy chains is a requirement for columnar mesophase formation.

TGA reveals good thermal stability for compound **IId** with an onset decomposition temperature (T_d) of 463°C and only 5% weight loss under nitrogen. As shown in table 1, all these compounds possess excellent thermal stability with T_d ranging from 441 to 463°C. Glass transition temperatures (T_g) could not be observed due to the small amount of energy involved.

Table 1. Transition temperatures (°C), enthalpy changes (kJ mol^{-1}) and decomposition temperatures (°C) of compounds **I** and **II** (**a**–**d**).

Compound	Transitions[a]	T_d[b]
I	Cr 142.8 I I 141.9 Cr	452
IIa	Cr 141.1 (43.6) I I 140.5 (−41.7) Cr	441
IIb	Cr_1 106.9 (8.5) Cr_2 130.4 (15.7) Cr_3 135.9 (5.2) I I 114.0 (broad) Col_h 111.9 (−24.4) Cr	445
IIc	Cr 136.1 (27.2) I Cr_1 73.3 (4.5) Cr_2 124.8 (25.6) I I 108.5 (−6.6) Col_h 93.4 (−11.2) Cr Cr 123.2 (56.2) I I 108.7 (−7.1) Col_h 92.8 (−11.3) Cr	454
IId	Cr_1 86.7 Cr_2 115.0 Col_h 140.1 (broad) I I 135.9 (−1.03) Col_h … …Col_h 137.2 (broad) I	463

[a]Transitions detected by DSC and optical microscopy (10°C min^{-1}).
[b]Thermogravimetric measurements, onset of decomposition under nitrogen (10°C min^{-1}).

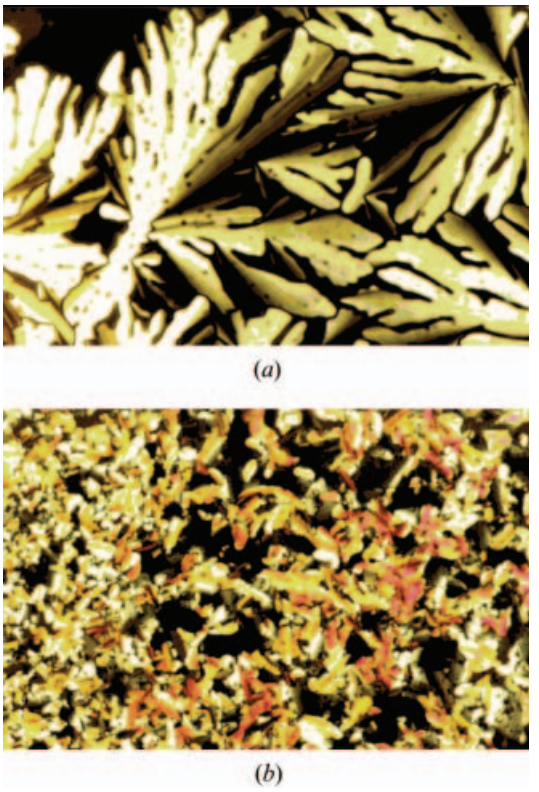


Figure 2. (*a*) The dendrite or platelet texture of compound **IId** at 139.3°C, just below the clearing point, on a glass substrate (×165). (*b*) The pseudo-focal-conic texture of compound **IId** at 139.0°C, on a glass substrate (×66).

Compound **IId** on cooling exhibited a dendritic growth from the isotropic liquid, with a dendrite or platelet texture (figure 2) typical for the formation of a hexagonal columnar phase. Upon annealing, the mesophase defects evolved to give a pseudo-focal-conic texture, characteristic of a hexagonal columnar mesophase (Col_h). The high viscosity of the phase is also consistent with a columnar mesophase. The similarities of the optical textures observed at temperatures above and below the melting point indicate that the columnar structure of the mesophase is retained at low temperature (presumably a glassy or crystalline solid). The material did not crystallize on further cooling, and showed only a transition to the isotropic liquid upon subsequent heating. It is difficult to determine by optical microscopy whether the hexagonal phase observed is disordered or ordered. By DSC, the first heating scan showed three peak endotherms: the first peak corresponds to the crystal-1 to crystal-2 transition at 86.7°C, the second peak corresponds to the crystal-2 to columnar mesophase transition at 115.0°C, and the third peak corresponds to the transition to the isotropic liquid at 140.1°C. On cooling, crystallization did not occur, but no glass transition was detected and only the peak related to isotropization was observed on scans after further heating to 137.2°C. However, when the DSC scan was repeated after one week, the peak corresponding to the melting of the material was again observed, showing that crystallization of the compound takes place when it is allowed to stand for a long period of time.

3.3. *Optical study*

All optical data are summarized in table 2 and representative absorption and emission spectra for **I** and **IId** in chloroform solution are shown in figure 3. Absorption and emission spectra for **I** and **II** in chloroform solution are dominated by intense bands peaking in the ranges 305 to 318 nm and 366 to 382 nm, respectively. All the compounds exhibit essentially the same absorption profile: an intense, low lying (near UV region) and structureless absorption band. The large molar absorption coefficients ($\varepsilon \geqslant 30\,000\,M^{-1}\,cm^{-1}$) are indicative of highly π–conjugated systems. Because of the intensities and their similarity to the absorption band of other 1,3,4-oxadiazole systems [12], the band is attributed to spin-allowed π–π* transitions involving the phenyloxadizole framework. Compound **I** is seen to undergo a slight hipsochromic shift of the absorption

Table 2. Summaries of physical measurements of compounds **I** and **II** (**a**–**d**).

	Absorption[a]	Emission[a,b]			
Compound	$\lambda_{abs\ max}$/nm	$\lambda_{em\ max}$/nm	Stokes shift/nm	Φ_{PL}[c]	τ_f/ns
I	305	366	61	0.050	1.24
IIa	317	376	59	0.454	1.55
IIb	317	376	59	0.452	1.56
IIc	317	376	59	0.472	1.54
IId	318	382	64	0.436	τ_1=0.59; τ_2=8.68

[a]Measured in $CHCl_3$.
[b]Excited at absorption maxima.
[c]Standard quinine sulphate (Φ_f=0.546) in 1M H_2SO_4.

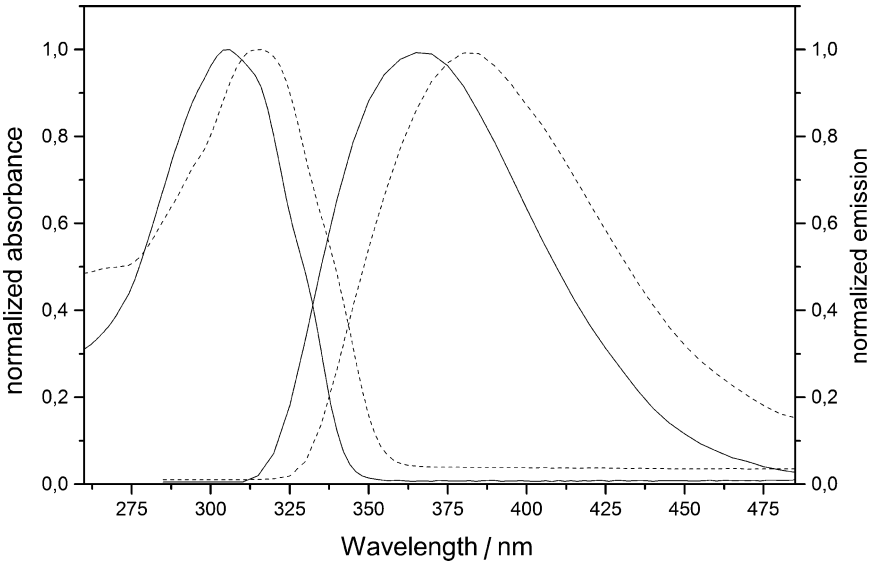


Figure 3. Normalized absorption and emission spectra of compounds **I** (solid lines) and **IId** (dashed lines) in chloroform solution.

and emission maxima with a smaller aromatic core (λ_{abs}=305 nm and λ_{em}=366 nm for **I** to λ_{abs}=318 nm and λ_{em}=382 nm for **IId**). The absorption and fluorescence of **II(a–d)** exhibit the same features and show no significant shifts of the absorption and emission maxima wavelength.

Photoluminescence is observed for all the compounds in solution with quantum yields (Φ_{PL}) of 5% for **I** and 45% (average) for **II**. The only noticeable variations in absorption and emission maxima are a bathochromic shift of the maxima wavelengths for compounds **II(a–d)** compared with **I** ($\Delta\lambda_{abs}$=12 nm and $\Delta\lambda_{em}$=10–16 nm). Such a red shift is consistent with the fact that for compounds **II** there is threefold symmetry with phenyloxadiazole units, which enhances the π–electron delocalization along the unsaturated system. Another characteristic of the fluorescence of **II(a–c)** is that their luminescence decay is mono exponential (1.6 ns). Compound **IId** exhibits an intense luminescence at room temperature in chloroform solution (λ_{em}=382 nm) and the luminescence decay is biexponential (τ_1=0.59; τ_2=8.68). On the basis of lifetimes and quantum yields, the luminescence of all the compounds is attributed to π–π* fluorescence.

4. Conclusions

We have synthesized a new class of 1,3,4-oxadiazole derivatives that form columnar mesophases over a large temperature range. Liquid crystalline 1,3,4-oxadiazole derivatives are proposed as potential charge-carrier-mobility columnar materials. The photoluminescence, another property exhibited by all the compounds, may be used for LED designing, as will be discussed in a future paper.

Acknowledgements

We gratefully acknowledge partial financial support of this work from the CNPq and PRONEX (Brazil). We thank Dr Miguel S. B. Caro and co-workers for recording NMR spectra and for helpful discussions. Dr Frank Quina (IQ-USP) is thanked for useful discussions and free access to photophysical instruments.

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