New liquid crystals derived from thiophene connected to the 1,2,4-oxadiazole heterocycle

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ABSTRACT

In this study, eight new compounds derived from thiophene were synthesised and characterised. The four symmetrical compounds contain two heterocyclic 1,2,4-oxadiazole on each side of the 2,5-disubstituted thiophene, and the four non-symmetrical compounds contain alkyne groups as a spacer replacing one of these heterocycles. Some of the compounds presented liquid crystalline properties with smectic and nematic mesophases. The non-symmetrical compounds presented low emission of blue light.

Introduction

Over the past few decades liquid crystals (LCs) have received special attention due to the possibility of reorientation with electric and magnetic fields [1,2], which allows control of their self-organising ability [3–5]. Thus, these materials have become good candidates for technologic application in electro-optic displays, in solar cells [6], as sensors [7], for high-density memory storage [8] and in light-emitting diodes (OLEDs) [9].

The design of new molecules is important to gaining a better understanding of the mesophase formation and the influence on the LC properties. Heterocycles with five-ring members have displayed non-linearity and less mesogenic stability [10–15]. However, these heterocycles generally have heteroatoms (N, O, S) in their structure, giving the molecules a longitudinal dipole moment, which can induce interesting liquid crystal properties [10,16]. There are many reports in the literatures on 1,2,4-oxadiazole heterocycle derivatives with good thermal stability and emission in the blue region of the visible electromagnetic spectrum [17–20]. Liquid crystalline compounds can present interesting optical and mesomorphic properties influenced by the curvature [21–26].

Studies on the 1,2,4-oxadiazole heterocycle connected to thiophene, which presents liquid crystals properties, appear to be absent from the literature. Thus, eight new compounds of the 1,2,4-oxadiazole...
heterocycle derivatives were synthesised and characterised. Four symmetrical molecules were designed by changing the number of chains (Scheme 1) and to the four asymmetrical molecules a triple bond was added (Scheme 2). Some of the compounds presented liquid crystalline properties, with smectic C (SmC) and nematic (N) mesophases.

**Measurements and characterisation**

$^1$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 discs or films. Mass spectra were recorded on a Bruker microOTOF-Q II APCI-Qq-TOF mass spectrometer.

The textures of the mesophases were captured by polarising 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 a DSCQ2000 calorimeter. Thermogravimetric analysis (TGA) was carried out using a Shimadzu analyser with the TGA-50 module. The X-ray diffraction (XRD) analysis was performed on a XPERTPRO (PANalytical) diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and the applied power was 1.2 kVA. The sample was prepared by prior heating of the powder over a glass plate (using a hot stage) until complete melting, followed by solidification on cooling, forming a uniform film of around 1 mm thickness. The scan was carried out in continuous mode from 2° to 30° ($2\theta$).
angle) with the sample 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 were recorded in solution on a Hitachi-F-4500. The relative fluorescence quantum yields ($\Phi_F$) were determined according to a published method [27].

Results and discussion

Synthesis

The synthesis procedures of the symmetrical compounds 8a–d are illustrated in Scheme 1. First, the thiophene 1 was carefully iodinated using molecular I$_2$. The dinitrile 3 was obtained through a nucleophilic substitution using copper cyanide. The intermediate 4 was then synthesised by reacting dinitrile 3 with NH$_2$OH.HCl, NaOH and ethanol. The alkylated acids 6a–d were obtained using the same synthetic route. The commercial carboxylate acids 5a–d were esterified via the Fischer reaction, using ethanol as the solvent and the reactant in the presence of sulfuric acid as a catalyst. The esters were then O-alkylated by Williamson etherification, using the 1-bromodecane, K$_2$CO$_3$ and butanone as the solvent. The catalyst TBAB (tetrabutylammonium bromide) was used for the alkylation of the compounds with two or more hydroxyl groups. The esters were saponified affording the carboxylic acids 6a–d. The acid chlorides 7a–d were obtained using SOCl$_2$ and reacted with dioxime 4 in pyridine to form the final compounds 8a–d.

The synthetic route used to obtain the asymmetrical compounds 13a–d is illustrated in Scheme 2. Compound 9 was previously synthesised according to the literature [28] and then reacted with the intermediate 2 through Sonogashira coupling, affording compound 10. The nitrile 10 was obtained through a nucleophilic substitution using copper cyanide, the nitrile group being converted to the oxime group 12. The oxime 12 was reacted with the acid chlorides 7a–d to form the oxadiazoles 13a–d.

All compounds were characterised by IR and $^1$H and $^{13}$C NMR spectroscopy (with the exception of compound 8a, which was not characterised by $^{13}$C NMR due to its low solubility in deuterated solvents) and mass spectroscopy.

Thermal behaviour

The thermal properties of the final compounds were investigated by polarising optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are reported in Table 1. All of the compounds presented good thermal stability, with decomposition temperatures above 300°C. Only compounds 8a and 13a presented LC behaviour. Figure 1 shows the thermograms for compound 13a, where three reversible transitions are clearly seen. On heating, the first endotherm peak at 96.6°C (37.5 kJ/mol) with high enthalpy indicates a transition from solid state to an LC mesophase. The second and third endothermic transitions at 127.7°C (1.8 kJ/mol) and

![Scheme 2. Synthetic route of unsymmetrical compounds 13a–d: (i) PdCl$_2$(PPh$_3$)$_2$, Cul, Et$_3$N, PPh$_3$, (92%); (ii) CuCN, DMF, (64%); (iii) NH$_2$OH.HCl KOH, MeOH, (94%); (iv) (dry) pyridine, 7a–d (66–75%).]
163.6°C (2.3 kJ/mol) presented lower associated enthalpy, which indicates transitions between distinct mesophases and to the isotropic state. The DSC thermograms for compound 8a are available in the supporting information.

The thermal behaviour obtained by DSC is consistent with the data observed by POM, where it was possible to identify the LC character of the mesophases. The observation by POM was performed with slight heating to the isotropic temperature and subsequent cooling to the crystallisation temperature at a rate of 5°C/min. This procedure was adopted for all compounds. Compound 8a displayed a droplet texture, which coalesced into a schlieren texture with four-fold defect domains. Further cooling resulted in the appearance of a marble texture. The schlieren, droplet and marble textures clearly indicate a nematic mesophase. Figure 2(c) shows, for compound 13a, the moment when the transition from an isotropic liquid to a fluid mesophase occurs, which is characteristic of nematics. As the sample is cooled it evolves a schlieren texture, which is also characteristic of SmC (Figure 2(d)).

Based on the above described studies on the triazole derivatives, it was possible to establish that the chemical structure strongly influences the existence of mesomorphism. Replacing a heterocycle with C≡C bonds caused a lowering of the melting point and the appearance of the mesophase SmC, along with an increase in the mesomorphic range. The compounds with only a para-substituent, with a total of two alkoxy chains, presented liquid crystal properties. Compounds with more than two alkoxy chains did not show mesomorphic behaviour. The absence of mesomorphism is probably related to the increased number of alkoxy chains, which hinders the free rotation of molecules in the layer caused by an increased volume, this being unfavourable for the appearance of the liquid-crystal properties [29–31].

### X-ray diffraction studies

XRD experiments were carried out on compound 13a to investigate the smectic structure exhibited by the mesophase. The XRD pattern for compound 13a (Figure 3) shows two reflection peaks \( d_{001} = 30.4 \text{ Å} \) and \( d_{002} = 15.3 \text{ Å} \) at the low-angle region with a ratio of \( d_{001} / d_{002} \approx 2 \), which confirms a smectic organisation [30,32]. The diffuse peak observed in the region of \( 2\theta = 4.4 \) degrees is assigned to the lateral distance between the neighbouring molecules within the layers [33,34]. Comparing the first diffraction peak \( d_{001} \), which corresponds to the interlayer spacing, to the molecular length \( L = 36.2 \text{ Å} \) (estimated by ChemBio3D Ultra Software, version 11.0.1.), one can infer that the aliphatic chains are folded or the molecules are tilted within the layers. Considering the molecules in the most extended form, the tilt angle was calculated using the relationship \( \cos \theta = d_{100} / L \) and a value of \( \theta = 33 \) degrees was obtained, which is consistent with the values for the SmC phases [35].

### Optical properties

The symmetrical compounds 8a–d do not display fluorescence. However, after modification of the 1,2,4-oxadiazole heterocycle with the triple bond, the

### Table 1. Transition temperatures (°C), enthalpy changes (kJ mol\(^{-1}\)) and decomposition temperatures (°C) for the final compounds.

| Comp. | Transitions a | \( T_{\text{decomposition}} \) b |
|-------|---------------|-------------------------------|
| 8a    | Cr 184 (59.8) N 189 (1.0) I | 338 |
|       | I 186 (0.9) N 161 (55.6) Cr |
| 8b    | Cr 107 (63.3) I | 319 |
| 8c    | Cr 60.6 (87.8) I | 361 |
| 8d    | Cr 61 (90.7) I | 363 |
| 13a   | Cr 96.6 (37.5) SmC 127.7 (1.8) N 163.6 (2.3) I | 312 |
|       | I 163.2 (2.1) N 127.5 (1.8) SmC 79.3 (39.3) Cr |
| 13b   | Cr 124.1 (38.8) I | 342 |
|       | I 117.1 (36.5) Cr |
| 13c   | Cr 22.8 (17.5) I | 333 |
|       | I 7.61 (15.2) Cr |
| 13d   | Cr 37.4 (29.5) I | 349 |
|       | I 25.9 (13.7) Cr |

a Transition determined by DSC and POM at a scan rate of 10°C min\(^{-1}\). SmC = smectic C mesophase; Cr = Crystal phase; I = Isotropic liquid.

b Determined by TGA, thermogravimetric measurements referring to the beginning of decomposition under nitrogen atmosphere.

**Figure 1.** (colour online) Thermogram obtained by DSC analysis of the second heating and cooling cycles at 10°C min\(^{-1}\) showing the thermal transitions of compound 13a.
compounds 13a–d became luminescent. This substitution probably provided a higher conjugation of the molecules.

The absorption and emission studies of the asymmetrical 13a–c compounds were carried out in chloroform solution at $10^{-5}$ M (Figure 4). The absorption spectra are very similar, with a maximum centred at around 332 nm. The molar absorptivity of these compounds was in the range of 21,000–26,000 L mol$^{-1}$cm$^{-1}$, attributed to $\pi-\pi^*$ transitions. These compounds present fluorescence in the blue region of the visible spectrum with maxima at around 400 nm. However, they are poor fluorophores with fluorescence quantum yields ($\Phi_F$) in the range of 0.19–0.24. The Stokes shift remained between 59–76 nm.

Figure 2. (colour online) POM micrographs of compounds 8a and 13a formed upon cooling from the isotropic phase (33x magnification): (a) schlieren texture at 186°C and (b) marble texture at 182°C of compound 8a; and (c) formation of nematic mesophase at 162°C and (d) transition stripes at nematic–smectic C phase transition during the temperature decrease, 127.5°C, of compound 13a.

Figure 3. XRD pattern of compound 13a at 110°C in the SmC mesophase.
Table 2. Spectroscopic (UV–vis and fluorescence) properties of the asymmetrical compounds 13a–d.

| Comp. | Absorption $^a$ ($\lambda_{max}$/nm) | Emission $^a$ ($\lambda_{max}$/nm) | $\varepsilon$/10$^3$ (L mol$^{-1}$ cm$^{-1}$) | Stokes Shift (nm) | $\Phi$ $^b$ |
|-------|----------------------------------|----------------------------------|---------------------------------|----------------|--------|
| 13a   | 340 399                            | 399 2.1                          | 59 0.23                        |                |        |
| 13b   | 326 399                            | 399 3.2                          | 73 0.24                        |                |        |
| 13c   | 339 400                            | 400 2.2                          | 61 0.19                        |                |        |
| 13d   | 324 400                            | 400 2.6                          | 76 0.20                        |                |        |

$^a$ Determined in CHCl$_3$ solution (1.0 × 10$^{-5}$ M)

$^b$ Excited at the wavelength of maximum absorption in CHCl$_3$ solution, fluorescence in CHCl$_3$ solution using PBD ($\Phi_e = 0.83$) as the standard.

Figure 4. Absorption and emission spectra for chloroform solutions (1.0 × 10$^{-3}$ M) of compounds 13a–d.

Conclusions

A new series of compounds derivative from thiophene connected to the 1,2,4-oxadiazole heterocycle were synthesised. Liquid crystal behaviour (smectic and nematic) was observed for two of the compounds obtained. On increasing of the number of chains in the asymmetrical and non-asymmetrical compounds the mesomorphic behaviour is not favoured, probably due to an increase in the volume. The insertion of the triple bond as a spacer, replacing one of the oxadiazole heterocycles, in the case of the non-symmetrical compounds, allows the lowering of the melting point and the appearance of the more organised SmC mesophase. The symmetrical compounds do not present fluorescence properties, however the non-symmetrical compounds with triple bonds show fluorescence in the blue region of the visible spectrum.

Experimental

Compounds 2, 6a–d and 10 were synthesised according to procedures described in the literature [31,36].

Thiophene-2,5-dicarbonitrile (3). In the first step, 5.0 g (15 mmol) of 2,5-diiodothiophene 2 in 30 mL of dimethylformamide were placed into a 120 mL flask equipped with a condenser. The solution was heated to 100°C and 3.4 g (37 mmol) of copper cyanide were added. The suspension was stirred and refluxed for over 8 h. Next, 2.0 g (8 mmol) of FeCl$_3$.6H$_2$O in 50 mL of a solution of hydrochloric acid (1.7 mol/L) were added at room temperature and the mixture was stirred for 30 min. The suspension was filtered off and the solid was washed with 30 mL of CH$_2$Cl$_2$. The solution was then extracted with CH$_2$Cl$_2$ (3 × 50 mL) and washed with 30 mL of a saturated solution of Na$_2$SO$_4$. The organic phase was dried using NaSO$_4$ and the solid was removed by rotatory evaporation. The solid was purified by column chromatography on silica, with hexane/ethyl acetate (90/10) as the eluent, affording 3.7 g (60%) of a yellow solid. Mp: 99–101°C. (IR KBr pellet) $\nu_{max}$ cm$^{-1}$. 3107, 3097, 2229, 1631, 1436. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$, ppm: 7.63 (s, 2H, Ar-H), 13C NMR (CDCl$_3$), $\delta$, ppm: 137.2, 116.4, 112.1.

Thiophene-2,5-diamidoxime (4). First, 1.0 g (7.6 mmol) of compound 3, 1.3 g (18.3 mmol) NH$_3$.HCl and 80 mL of methanol were placed in a 250 mL flask. The suspension was cooled in an ice/water bath and 0.7 g (18.3 mmol) of NaOH was added. The solution was stirred for 30 min at room temperature and the temperature was then increased slowly and then the solution was refluxed for 5 h. The solvent was removed by rotatory evaporation and the solid was recrystallised from water affording 1.3 g (85%) of a beige solid. Mp: 219 dec°C. IR (KBr pellet) $\nu_{max}$ cm$^{-1}$. 3480, 3452, 3379, 2887, 1665, 1597. $^1$H NMR (DMSOd$_6$, 400 MHz), $\delta$, ppm: 9.68 (s, 2H, −OH), 7.33 (s, 2H, Ar-H), 5.28 (s, 4H, −NH$_2$). $^{13}$C NMR (CDCl$_3$), $\delta$, ppm: 148.0, 136.9, 125.1.

The final compounds (1,2,4-oxadiazoles derivatives 8b–d) were synthesised according to the procedure described for compound 8a.

2,5-bis(5-(4-(decyloxy)phenyl)-1,2,4-oxadiazol-3-yl)thiophene (8a). First, 1.2 g (4.4 mmol) of compound 6a and 5.0 mL of SOCl$_2$ were placed into a 50 mL flask equipped with a condenser and a tube with a drying agent (CaCl$_2$). The solution was stirred for 7 h at 60°C. The excess thionyl chloride was removed by rotatory evaporation and then 20 mL of dry pyridine and 0.4 g
(2.0 mmol) of compound 4 were added. This solution was then maintained under reflux for 20 h. The solution was poured into 100 mL of water/ice and the solid was filtered off and washed with lots of water. A beige solid (1.1 g, 84%) was obtained by recrystallisation in CHCl3. Mp: 60.6°C. IR (KBr pellet) \( \nu_{max} \text{cm}^{-1}: \) 3093, 2921, 2852, 1607,1576. 1H NMR (CDCl3), \( \delta \), ppm: 8.16 (d, \( J = 8.9 \) Hz, 4H, Ar-H), 7.90 (s, 2H, Ar-H), 7.05 (d, \( J = 8.9 \) Hz, 4H, Ar-H), 4.06 (m, 4H, –OCH2–), 1.84 (m, 4H, –CH2–), 1.49 (m, 4H, –CH2–), 1.28 (m, 24H, –CH2–), 0.89 (t, \( J = 6.8 \) Hz, 6H, –CH3). Q-TOF/MS: Calcd: m/z 685.3790 (M + H)+. Found: m/z 685.3782 [(M + H)+, 100%].

5-(4-(decyloxy)phenyl)ethyl)thiophene-2-carboxylic acid (11). Compound 11 was synthesised according to the procedure described for compound 3. It was purified by column chromatography on silica, using hexane as the eluent, affording 0.38 g (64%) of a brown solid. Mp: 189°C. IR (KBr pellet) \( \nu_{max} \text{cm}^{-1}: \) 138-140°C. IR (KBr pellet) \( \nu_{max} \text{cm}^{-1}: \) 3093, 2921, 2850, 2217, 1970, 1604. 1H NMR (CDCl3, 400 MHz), \( \delta \), ppm: 7.50 (d, \( J = 8.6 \) Hz, Ar-H), 7.16 (d, 1H, \( J = 3.9 \) Hz, Ar-H), 6.89 (d, 2H, \( J = 8.8 \) Hz, Ar-H), 3.97 (t, \( J = 6.3 \) Hz, 2H, –OCH2–), 1.78 (m, 2H, –CH2–), 1.45 (m, 2H, –CH2–), 1.26 (m, 12H, –CH2–), 0.88 (t, \( J = 7.0 \) Hz, 3H, –CH3). 13C NMR (CDCl3), \( \delta \), ppm: 160.0, 137.2, 133.3, 131.3, 130.8, 114.7, 113.8, 113.2, 169.3, 97.2, 79.4, 68.2, 31.9, 29.7, 29.6, 29.5, 29.5, 29.1, 26.0, 22.7. 1H NMR (DMSOd6, 400 MHz), \( \delta \), ppm: 9.82 (sl, 1H, –NOH), 7.47 (d, \( J = 8.8 \) Hz, 2H, Ar-H), 7.43 (d, 1H, \( J = 3.9 \) Hz, Ar-H), 7.28 (d, 1H, \( J = 3.9 \) Hz, Ar-H), 6.97 (d, 2H, \( J = 8.8 \) Hz, Ar-H), 6.03 (sl, 1H, –NH2), 3.99 (t, \( J = 6.4 \) Hz, 2H, –OCH2–), 1.70 (m, 2H, –CH2–), 1.40 (m, 2H, –CH2–), 1.24 (m, 12H, –CH2–), 0.85 (t, \( J = 6.8 \) Hz, 3H, –CH3). RMN 13C (CDCl3) \( \delta \) ppm: 159.6, 147.5, 138.3, 133.4, 132.4, 125.5, 115.3, 113.8, 94.3, 81.7, 68.1, 31.9, 29.5, 29.5, 29.4, 29.2, 29.0, 25.9, 22.6, 14.4.

The non-symmetrical compounds (1,2,4-oxadiazole 13b-d) were synthesised according to the procedure described for compound 13a.

5-(4-(decyloxy)phenyl)-3-(5-((4-(decyloxy)phenyl)ethyl)thiophene-2-carboxylic acid (13a). Firstly, 0.24 g (0.88 mmol) of compound 6a and 5 mL of thionyl chloride were placed into a 50 mL flask equipped with a condenser and a tube with drying agent (CaCl2). The solution was stirred for...
5 h at 70°C. The excess thionyl chloride was removed in the rotary evaporator and 0.25 g (0.63 mmol) of amidoxime 12 and 20 mL of dry pyridine were then added. The mixture was stirred for 24 h under reflux and then poured into 100 mL of water/ice. The solid was filtered off and purified by column chromatography on silica, with hexane/ethyl acetate (95/5) as the eluent, affording 0.30 g (75%) of the beige solid. Mp: 96.6°C – SmC 127.7°C – N 163.6°C – I. IR (KBr pellet) νmax cm⁻¹: 2921, 2850, 2370, 2198, 1610. ¹H NMR (400 MHz, CDCl₃), δ, ppm: 8.13 (d, J = 8.6 Hz, 2H, Ar-H), 7.73 (d, J = 3.9 Hz, 1H, Ar-H), 7.47 (d, J = 8.6 Hz, 2H, Ar-H), 7.25 (1H, Ar-H), 7.02 (d, J = 8.6 Hz, 2H, Ar-H), 6.89 (d, J = 8.8 Hz, 2H, Ar-H), 4.04 (t, J = 6.4 Hz, 2H, –OCH₂–), 3.97 (t, J = 6.4 Hz, 2H, –OCH₂–), 1.80 (m, 4H, –CH₂–), 1.56 (m, 4H, –CH₂–), 1.27 (m, 24H, –CH₂–), 0.88 (t, J = 6.6 Hz, 6H, –CH₃). ¹³C NMR (CDCl₃), δ, ppm: 175.6, 171.2, 164.4, 163.0, 159.7, 133.1, 131.9, 130.1, 129.3, 127.4, 116.1, 115.0, 114.6, 114.2, 95.5, 85.8, 68.4, 68.1, 31.9, 29.6, 29.3, 29.1, 26.0, 22.7, 14.1. Q-TOF/MS: Calcd: m/z 641.3771 [(M + H)+, 100%]. Found: m/z 641.3771 [(M + H)+, 100%].

5-(3,4-bis(decyloxy)phenyl) (ethynyl)thiophen-2-yl)-1,2,4-oxadiazole (13b). Compound 13b was purified by column chromatography on silica, with hexane/ethyl acetate (90/10) as the eluent, affording 0.62 g (70%) of a beige solid. Mp: 175.6, 171.2, 164.4, 163.0, 159.7, 133.1, 131.9, 130.1, 129.3, 127.4, 116.1, 115.0, 114.6, 114.2, 95.5, 85.8, 68.4, 68.1, 31.9, 29.6, 29.3, 29.1, 26.0, 22.7, 14.1.

Q-TOF/MS: Calcd: m/z 641.3771 [(M + H)+, 100%].

5-(3,4-bis(decyloxy)phenyl)-3-(5-((4-(decyloxy)phenyl)ethynyl)thiophen-2-yl)-1,2,4-oxadiazole (13c). Compound 13c was purified by column chromatography on silica, with hexane/ethyl acetate (90/10) as the eluent, yielding 0.62 g (70%) of a beige solid. Mp: 22.8°C. IR (KBr pellet) νmax cm⁻¹: 2923, 2852, 2372, 1629. ¹H NMR (400 MHz, acetone-d₆), δ, ppm: 7.81 (d, J = 3.9 Hz, 1H, Ar-H), 7.52 (d, J = 8.9 Hz, 2H, Ar-H), 7.41 (d, J = 3.9 Hz, 1H, Ar-H), 7.28 (d, J = 2.3 Hz, 2H, Ar-H), 7.01 (d, J = 8.9 Hz, 2H, Ar-H), 6.79 (t, J = 2.3 Hz, 1H, Ar-H), 4.11 (t, J = 6.4 Hz, 4H, –OCH₂–), 4.05 (t, J = 6.4 Hz, 2H, –OCH₂–), 1.80 (m, 6H, –CH₂–), 1.51 (m, 6H, –CH₂–), 1.29 (m, 36H, –CH₂–), 0.88 (m, 9H, –CH₃). ¹³C NMR (acetone-d₆), δ, ppm: 164.3, 161.0, 160.1, 133.1, 132.4, 131.7, 129.9, 128.6, 127.2, 125.1, 114.9, 114.8, 106.1, 106.0, 95.7, 80.1, 68.3, 67.9, 31.7, 29.4, 29.2, 25.8, 22.4, 13.5.

Q-TOF/MS: Calcd: m/z 797.5286 [(M + H)+. Found: m/z 797.5285 [(M + H)+, 100%].

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Disclosure statement

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References

[1] Wang M, He L, Zorba S, et al. Magnetically actuated liquid crystals. Nano Lett. 2014;14:3966–3971. doi:10.1021/nl501302s.
[2] Zhang Y, Liu Q, Mundoor H, et al. Metal Nanoparticle dispersion, alignment, and assembly in nematic liquid crystals for applications in switchable Plasmonic color filters and E-polarizers. ACS Nano. 2015;9:3097–3108. doi:10.1021/nn5074644.

[3] Westphal E, Prehm M, Bechtold IH, et al. Room temperature columnar liquid crystalline phases of luminescent non-symmetric star-shaped molecules containing two 1,3,4-oxadiazole units. J Mater Chem C. 2013;1:8011–8022. doi:10.1039/c3tc31704h.

[4] Goodby JW. Editorial – liquid crystals. Chem Soc Rev. 2007;36:1855–1856.

[5] Merlo AA, Braun JE, Vasconcelos U, et al. Chiral liquid crystalline m-nitrotolans and tolans: synthesis and mesomorphous properties. Liq Cryst. 2000;27:657–663. doi:10.1080/026782900202516.

[6] Li F, Chen W, Chen Y. Mesogen induced self-assembly for hybrid bulk heterojunction solar cells based on a liquid crystal D-A copolymer and ZnO nanocrystals. J Mater Chem. 2012;22:6259–6266. doi:10.1039/c2jm16853g.

[7] Sen A, Kupcho KA, Grinwald BA, et al. Liquid crystal-based sensors for selective and quantitative detection of nitrogen dioxide. Sens Actuators B. 2010;152:164–170. doi:10.1016/j.snb.2010.06.014.

[8] Hara M, Nagano S, Seki T. π-π Interaction-induced vertical alignment of silica mesochannels templated by a discotic lyotropic liquid crystal. J Am Chem Soc. 2010;132:13654–13656. doi:10.1021/ja106220j.

[9] Wang L, He W, Wang M, et al. Effects of symmetrically 2,5-disubstituted 1,3,4-oxadiazoles on the temperature range of liquid crystalline blue phases: a systematic study. Liq Cryst. 2013;40:354–367. doi:10.1080/02678292.2012.749306.

[10] Benbayer C, Saidi-Besbes S, Grelet E, et al. Structure–property study of new [1,2,3]-triazole liquid crystalline derivatives. Liq Cryst. 2013;40:1520–1528. doi:10.1080/02678292.2013.822111.

[11] Merlo AA, Gallardo H, Taylor TR. Cristais Líquidos Ferroelétricos – CLF. Uma abordagem sintética. Quim Nova. 2001;24:354–362. doi:10.1590/S0100-404220010003000012.

[12] Ely F, Conte G, Merlo AA, et al. A new synthetic approach based on (−)-menthone for chiral liquid crystals. Liq Crys. 2004;31:1413–1425. doi:10.1080/02678290412331293440.

[13] Bartulin J, Martinez R, Gallardo H, et al. Synthesis and mesomorphous properties of 3,5-bis-(p-n-alkoxyphenyl) isoxazole and 3,5-bis-(p-n-alkoxyphenyl)pyrazole. Mol Cryst Liq Cryst. 1993;225:175–182. doi:10.1080/10587259308036227.

[14] Gallardo H, Conte G, Tuzimoto PA, et al. New luminescent liquid crystals based on 2,1,3-benzothiadiazole and bent five-membered N-heterocyclic cores. Liq Cryst. 2012;39:1099–1111. doi:10.1080/02678292.2012.698313.

[15] Vieira AA, Bryk FR, Conte G, et al. 1,3-Dipolar cycloaddition reaction applied to synthesis of new unsymmetric liquid crystal compounds-based isoxazole. Tetrahedron Lett. 2009;50:905–908. doi:10.1016/j.tetlet.2008.12.021.

[16] Subrao M, Bhagavath P, Bhat SG, et al. Four ring achiral ferroelectric liquid crystals of 1,2,4-oxadiazoles: synthesis and characterisation. Liq Cryst. 2016;43(3):400–410.

[17] Agneeswari R, Tamilavan V, Song M, et al. Synthesis of polymers containing 1,2,4-oxadiazole as an electron-acceptor moiety in their main chain and their solar cell applications. J Polym Sci Part A: Polym Chem. 2013;51:2131–2141. doi:10.1002/pola.26605.

[18] Li Q, Cui LS, Zhong C, et al. Asymmetric design of bipolar host materials with novel 1,2,4-Oxadiazole unit in blue phosphorescent device. Org Lett. 2014;16:1622–1625. doi:10.1021/ol5002494.

[19] Gallardo H, Ferreira M, Vieira AA, et al. Columnar mesomorphism of bent-rod mesogens containing 1,2,4-oxadiazole rings. Tetrahedron. 2011;67:9491–9499. doi:10.1016/j.tet.2011.10.019.

[20] Westphal E, Silva DHD, Molin F, et al. Pyridinium and imidazolium 1,3,4-oxadiazole liquid crystals: a thermal and photophysical systematic investigation. RSC Adv. 2013;3:6442–6454. doi:10.1039/c3ra23456h.

[21] Gallardo H, Westphal E. Importance of organic synthesis in the development of liquid crystals. Curr Org Synth. 2015;12:806–821. doi:10.2174/1570179141206150828113416.

[22] Hernández-Ainsa S, Barberá J, Marcos M, et al. Liquid crystalline ionic dendrimers containing luminescent oxadiazole moieties. Macromolecules. 2012;45:1006–1015. doi:10.1021/ma202051c.

[23] Gallardo H, Bryk FR, Vieira AA, et al. Optical and thermal properties of unsymmetrical liquid crystalline compounds based on isoxazole. Liq Cryst. 2009;36:839–845. doi:10.1080/02678290903072035.

[24] Tuzimoto P, Santos DMPO, Moreira TD, et al. Luminescent liquid crystals containing a sulphur-based heterocyclic core. Liq Cryst. 2014;41:1097–1108. doi:10.1080/02678292.2014.903003.

[25] Subrahmanyan SV, Chalapathi PV, Mahabaleswara S, et al. Ferroelectric phases in non-symmetric achiral bent liquid crystals towards ambient temperatures: a novel series with oxadiazol as central moiety. Liq Cryst. 2014;41(8):1130–1151. doi:10.1080/02678292.2014.908478.

[26] Nguyen J, Wonderly W, Tauscher T, et al. The effects of lateral halogen substituents on the low-temperature cybotactic nematic phase in oxadiazole based bent-core liquid crystals. Liq Cryst. 2015;42(12):1754–1764. doi:10.1080/02678292.2015.1085599.

[27] Girotto E, Eccher J, Vieira AA, et al. Luminescent columnar liquid crystals based on 1,3,4-oxadiazole. Tetrahedron. 2014;70:3355–3360. doi:10.1016/j.tet.2013.09.079.

[28] Zhang ZL, Zhang LY, Shen ZH, et al. Synthesis and properties of mesogen-jacketed liquid crystalline polymers containing bistolane mesogen. J Polym Sci Part A: Polym Chem. 2010;48:4627–4639. doi:10.1002/pola.24216.

[29] Han J. 1,3,4-Oxadiazole based liquid crystals. J Mat Chem C. 2013;1:7779–7797. doi:10.1039/c3tc31458h.

[30] Perepichka IF, Perepichka DF, editors. Handbook of thiophene-based materials: applications in organic electronics and photonics. Volume two: properties and applications. Chichester: John Wiley & Sons Ltd; 2009.
[31] Girotto E Bechtold IH, Gallardo H. New Liquid Crystals Derived from Thiophene Connected to the 1,2,3-Triazole Heterocycle. Liq Cryst. 2015;42:1798–1807.

[32] Demus D, Goodby J, Gray GW, et al. Handbook of liquid crystals, Volume 1: Fundamentals. Weinheim: Wiley-VCH; 1998.

[33] Majumdar KC, Mondal S, Sinha RK. Synthesis and characterization of novel cholesterol based mesogenic compounds using ‘click’ chemistry. New J Chem. 2010;34:1255–1260. doi:10.1039/b9nj00744j.

[34] Rao DSS, Kumar MV, Prasad SK, et al. Novel columnar-calamitic phase sequences in a binary system of bent-core and rod-like mesogens. J Mat Chem C. 2013;1:7488–7497. doi:10.1039/c3tc31724b.

[35] Qu S, Chen X, Shao X, et al. Self-assembly of highly luminescent bi-1,3,4-oxadiazole derivatives through electron donor-acceptor interactions in three-dimensional crystals, two-dimensional layers and mesophases. J Mat Chem. 2008;18:3954–3964. doi:10.1039/b804189j.

[36] Lin YC, Lai CK, Chang YC, et al. Formation of hexagonal columnar phases by heterocyclic pyrimidine derivatives. Liq Cryst. 2002;29:237–242. doi:10.1080/02678290110097800.