New liquid crystals derived from thiophene connected to the 1,2,3-triazole heterocycle

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In this work, six new compound derivatives from thiophene were synthesised. The three symmetrical compounds were synthesised containing two heterocyclic 1,2,3-triazole on each side of thiophene, 2,5-disubstituted and the three non-symmetrical compounds were synthesised containing alkyne groups as a spacer in replacing one of these heterocycles. The structural modifications were made by changing the number of alkoxy groups in order to understand the relation between structure and mesomorphic behaviour. Some of the compounds presented liquid crystalline properties, smectic and nematic mesophases. The non-symmetrical compounds allowed for a low emission in the blue region.

\textbf{Keywords:} non-symmetrical compounds; terminal substituents; triple bond unit as spacer; XRD experiments; fluorescence quantum yields

Introduction

The chemistry of soft materials has been receiving a lot of attention in recent years such as polymers,\textsuperscript{1} gels,\textsuperscript{2} liquid crystals (LCs) \textsuperscript{3} and others.\textsuperscript{4,5} Especially, the LCs owing to increased technological applications with solar cells,\textsuperscript{6} sensors,\textsuperscript{7} high-density memory storage \textsuperscript{8} and organic light-emitting diodes.\textsuperscript{9} The LCs present the intrinsic ability of shelf assembling in organised structures,\textsuperscript{10} as smectic and columnar mesophases, which are driven by the molecular shape and intermolecular interactions.\textsuperscript{11,12}

The structure of these molecules and functional groups has a huge influence on the optical and mesomorphic properties of LCs.\textsuperscript{13} The insertion of double and triple bonds in organic molecules favours the formation of highly conjugate systems.\textsuperscript{14,15} As a result, it can induce and/or improve the luminescent properties presented by these materials,\textsuperscript{16,17} which are also important to their application in organic devices.\textsuperscript{18} Heterocycles also have a high influence on the physical properties of these materials, as derivatives of thiophene, 1,3,4-oxadiazole and 2,1,3-benzothiadiazole present high luminescence and good thermal stability.\textsuperscript{19–23} The 1,2,3-triazole heterocycle, in spite of the fact that the structural moiety itself does not occur in nature, is very important owing to the wide range of biological activities such as anti-HIV,\textsuperscript{24} anticancer activities and others.\textsuperscript{25} It has also been investigated for technological applications such as corrosion inhibitors,\textsuperscript{26} photographic materials \textsuperscript{27} and LCs.\textsuperscript{28}

LCs containing 1,2,3-triazole ring in their molecular structure have recently attracted much attention due to their interesting chemical and physical properties. Such properties include photoresponsive behaviour when the triazole ring is connected to azobenzene moiety \textsuperscript{29,30} and paramagnetism induced by the metal centre in Cu(II)-metallomesogen derivatives.\textsuperscript{31,32} Usually, 1,2,3-triazole ring is formed by a click reaction and studies have proved that its relative position inside the rigid core and the nature of the substituents attached to it induce dramatic effects on the mesomorphic behaviour.\textsuperscript{33} In addition, this five-membered ring can be used, for instance, to produce triazine-based disc-like LCs,\textsuperscript{34} where the molecules self-organised into columns with potential optoelectronic applications.

As far as we know, there are no reports in the literature of the 1,2,3-triazole heterocycle linked to thiophene presenting mesomorphic properties. As a result, this work synthesised six new compounds of 1,2,3-triazole derivatives, so that three symmetrical molecules were designed changing the number of chains (\textit{Scheme 1}), and the other three asymmetrical molecules where a triple bond was added (\textit{Scheme 2}). Some of the compounds presented liquid crystalline properties like smectic (SmC) and nematic (N) mesophases.

Measurements and characterisation

\textsuperscript{1}H and \textsuperscript{13}C NMR spectra were obtained with a Varian Mercury Plus 400 MHz instrument using...
tetramethylsilane as the internal standard. Infrared spectra were recorded on a PerkinElmer model 283 spectrometer using KBr discs or films. Mass spectra were recorded on a Bruker micrOTOF-Q II APCI-Qq-TOF mass spectrometer.

The textures of the mesophases were captured with a polarising optical microscope (POM), Olympus BX50 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 DSCQ 2000 calorimeter. Thermogravimetric analysis (TGA) was carried out using a Shimadzu analyzer with the TGA-50 module. The X-ray diffraction (XRD) experiment was carried out on an X’Pert-PRO (PANalytical) diffractometer using the linear monochromatic Cu Ka beam (λ = 1.5405 Å), with an applied power of 1.2 kVA. The sample was prepared using procedures described in the literature [35] with the heating and cooling of an amount of powder on a glass plate as substrate. The scans were performed in continuous mode from 2° to 30° (2θ 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

Scheme 1. Synthetic route derivatives of azide compounds 6a–c.

Scheme 2. Synthetic route of symmetrical compounds 11a–c.
fluorescence spectra in solution were recorded on a Hitachi-F-4500. The relative fluorescence quantum yields ($\Phi_F$) were determined according to a published method.[36]

Results and discussion

Synthesis

The intermediate compounds 6a–b were synthesised according to Scheme 1. Initially, the compounds 1a–b were done through nitration forming the 2a–b, through the catalytic reduction using Pd/C 10% obtaining amines 3a–b. After that, diazonium salt was formed through amines as described in the literature,[37] and in the next step the compounds 6a–b were formed by nucleophilic substitution using NaN$_3$. The intermediate compound 6c was obtained through unprotection of N-(4-(decyloxy)phenyl) acetamide (4) forming amine 5, and after it was done diazotisation and nucleophilic substitution giving the intermediate 6c.

The symmetrical compounds 11a–c were synthesised according to Scheme 2. Firstly, thiophene (7) was carried out by iodination using I$_2$ molecular. Compound 9 was obtained by sonogashira coupling [38] using the alkyne trimethylsilyl acetylene in the presence of a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ and CuI with Et$_3$N under N$_2$. Compound 9 was reacted with a catalytic amount of base in methanol to cleavage the trimethylsilyl groups, which resulted in the intermediate 10. The compounds target 11a–c were obtained by click reaction,[39] using a catalytic amount of CuI in ethanol/water and drops of triethylamine.

The synthetic route of the asymmetrical compounds 16a–c is presented in Scheme 3. Compound 12 was previously synthesised according to the literature,[40] then it was reacted with the intermediate 8 through sonogashira coupling, affording compound 13. A new sonogashira coupling was done to obtain the alcohol 14. Compound 14 was reacted with a catalytic amount of base in toluene to cleavage the tertiary alcohol group, resulting in the alkyne 15. The target compounds 16a–c were obtained by click reaction.

The structures of all the compounds were characterised by IR and $^1$H and $^{13}$C NMR spectra (with the exception of compounds 14a and 14b, which were not characterised by $^{13}$C NMR, due to low solubility in deuterated solvent) and mass spectroscopy.

Thermal behaviour

The thermal properties of final compounds were investigated by POM, DSC and TGA. The results are presented in Table 1.

TGA investigation of the symmetrical and asymmetrical compounds showed decomposition temperatures ranging between 285°C and 300°C. From the three symmetrical compounds, only compound 11c with six alkyl chains did not present liquid crystalline properties. Compound 11a presented mesomorphic properties at high temperatures; it was observed by POM that this material enters in the mesophase only at 271°C. Further increasing

![Scheme 3. Synthetic route of non-symmetrical compounds 16a–c.](image-url)
temperatures resulted in decomposition before reaching the isotropic phase; due to this fact, a better characterisation of this mesophase was not possible. Compound 11b showed monotropic behaviour. It was observed by POM the schlieren texture, with low fluidity, which resembles an SmC mesophase, but due to instability of the mesophase a better characterisation was not possible.

From the asymmetrical compounds 16a–c, only compound 16a displayed LC behaviour; the transition can be observed by the thermogram of Figure 1. It presented three exothermic transitions on heating; the first at 150.0°C (32.2 kJ mol⁻¹) with a high enthalpy value, indicating a transition from the solid state to SmC; the second at 195.4°C (1.2 kJ mol⁻¹) with a low enthalpy value, indicating SmC to N transition; and the third at 197.3°C (1.2 kJ mol⁻¹) also with a low enthalpy value, attributed to a N to isotropic transition. The same behaviour was observed on cooling, with the mesophases characterised by POM.

From the above-mentioned studies on the triazole derivatives, it was possible to establish that the chemical structure strongly influences the existence of mesomorphism. The final compounds presented a lower melting point with increasing number of chains and the asymmetric compounds containing the triple bond (16a–c) showed a lower melting point compared with the symmetrical ones (11a–c). Increasing the number of alkoxy chains, the appearance of mesomorphism was unfavourable, evident by the absence of liquid crystalline properties for compounds 11c (six alkoxy chains), 16b (three alkoxy chains) and 16c (four alkoxy chains) and the appearance of a very unstable mesophase for compound 11b (four alkoxy chains). Probably the increasing volume caused by the addition of alkyl chains was unfavourable to the appearance of the liquid crystalline properties.[41,42]

The mesophase exhibited by compound 16a was analysed by POM. The texture presented droplets characteristic of a nematic mesophase obtained on cooling compound 16a (Figure 2a). The micrograph in Figure 2b was identified as broken fan-shaped, characteristic of an SmC mesophase.

**Table 1. Transition temperatures (°C), enthalpy changes (kJ mol⁻¹) and decomposition temperatures (°C) of the final compounds.**

| Compound | Transitions | T_{dec}(onset) |
|----------|-------------|---------------|
| 11a      | Cr 240 (11.8) Cr’ 271 (16.6) SmX 280 (11.8) I | 285 |
| 11b      | Cr 77.2 (64.6) Cr’ 176.1 (77.6) I | 282 |
| 11c      | Cr 77.2 (78.3) Cr’ 121 (22.3) I | 293 |
| 16a      | Cr 150.0 (32.2) SmC 195.4 (1.2) N 197.3 (1.2) I | 297 |
| 16b      | Cr 124.1 (51.3) I I 117.1 (48.0) Cr | 303 |
| 16c      | Cr 77.2 (74.6) I I 26.9 (19.1) Cr | 300 |

Notes: SmX, unidentified mesophase; SmC, smectic C mesophase; Cr, crystal phase; I, isotropic liquid.

*Transition determined by DSC and POM at a scan rate of 10°C min⁻¹. bDetermined 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 cycle at 10°C min⁻¹ showing the thermal transitions of compound 16a.](image)
and $d_{002} = 17.3$ Å at the low-angle region with ratio $d_{001}/d_{002} \approx 2$, which confirms a smectic organisation. [43] The diffuse peak observed in the region of $2\theta = 4.6^\circ$ is assigned to the lateral distance between the neighbouring molecules within the layers.[44,45] Comparing the first diffraction peak $d_{001}$, which corresponds to the interlayer spacing, to the molecular length $L = 38.9$ Å (estimated by ChemBio3D Ultra Software, version 11.0.1, PerkinElmer Informatics, Inc., Waltham, MA, USA), the ratio $d_{001}/L = 0.87$ indicates that the aliphatic chains are folded or interdigitated or that 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 $\theta = 29^\circ$ was obtained, being in accordance with SmC phases.[46]

**Optical properties**

The symmetrical compounds 11a–c did not present fluorescence. However, after modification of the 1,2,3-triazole heterocycle by the triple bond, the compounds 16a–c became luminescent. This substitution probably provided a higher conjugation.

The absorption and emission studies of the asymmetrical 16a–c compounds were carried out in chloroform solution (Figure 4). The absorption spectra are very similar, with a maximum centred around 337 nm. The molar absorptivity of these compounds was in the range of 28,400–31,800 L mol$^{-1}$ cm$^{-1}$, attributed to $\pi-\pi^*$ transitions.[47] These compounds present fluorescence in the blue region of the visible spectrum with two main maxima around 380 and 398 nm, and an additional two shoulders around 343 and 360 nm. However, they are poor fluorophores with fluorescence quantum yields ($\Phi_F$) in the range of 0.14–0.19. The stokes shift remained between 42 and 44 nm. Through the optical studies, it was possible to observe that the variation of the alkyl chains did not result in significant changes in the properties of the asymmetrical compounds 16a–c. The results are summarised in Table 2.

**Conclusions**

A new series of compounds derivative from thiophene connecting to 1,2,3-triazole heterocycle were synthesised. Three compounds presented LC properties, with SmC and nematic mesophases. By increasing the number of alkoxy chains of the symmetrical and non-symmetrical compounds, the mesomorphic behaviour was unfavourable, probably occasioned by the increase in volume. It was observed that the insertion of the triple bond as a spacer replacing one of oxadiazol heterocycles for the non-symmetrical compounds allowed for the lowering of the melting point and the appearance of the more organised...
SmC mesophase. Finally, the non-symmetrical compounds allowed fluorescence in the blue region of the visible spectrum.

**Experimental**

**Synthesis of symmetrical compounds**

The compounds 6a–e were synthesised according to the literature.[39]

2,5-Diidothiophene (8). The solution of H₂O/HNO₃ (20/20 mL) was added slowly in 10.0 g (125 mmol) of thiophene 7, 31.8 g (125 mmol) of I₂ and 50 mL of CHCl₃, then it was refluxed for 24 h. The solution was extracted with CH₂Cl₂ (3 × 50 mL), the organic phase was washed with 100 mL of NaHNO₃, dried over anhydrous Na₂SO₄ and removed for rotary evaporation. The purification was by column chromatography on silica, hexane as eluent, affording 32.7 g of yellow solid (78%). Mp: 40–42°C. IR (KBr pellet) ν_{max} cm⁻¹: 3067, 1635, 1495. ¹H NMR (400 MHz, CDCl₃), δ, ppm: 6.94 (s, Ar-H). ¹³C NMR (CDCl₃), δ, ppm: 139.0, 76.5.

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2,5-bis((Trimethylsilyl)ethynyl)thiophene (9). Firstly, 5.0 g (14.9 mmol) of compound 8, 0.31 g (0.15 mmol) of PdCl₂(PPh₃)₂, 0.013 g (0.07 mmol) of CuI on 60 mL of Et₃N, and 3.54 g (56.9 mmol) of ethynyltrimethylsilane were added in 10 mL Et₃N. The mixture was stirred at 40°C for 13 h under an N₂ atmosphere. The mixture was cooled to room temperature and filtered off through a celite pad. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica, hexane as eluent, affording 3.96 g (96%) of yellow solid. Mp: 53–55°C. IR (KBr pellet) ν_{max} cm⁻¹: 2953, 2896, 2147. ¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.04 (s, 2H, Ar-H), 0.24 (s, 18H, –CH₃). ¹³C NMR (CDCl₃), δ, ppm: 132.8, 125.0, 100.4, 97.4, 0.3.

2,5-Diethynylthiophene (10). 3.9 g (1.4 mmol) of compound 9, 1 mol L⁻¹ KOH methanol solution (75 mL) was stirred at room temperature for 1 h. The reaction was followed by thin layer chromatography. The mixture was poured into water (25 mL) and extracted with hexane (3 × 35 mL). The organic phase was dried over anhydrous Na₂SO₄, then the solution was carefully evaporated under reduced pressure, affording black oil (81%). IR (KBr pellet) ν_{max} cm⁻¹: 3067, 1635, 1495. ¹H NMR (400 MHz, CDCl₃), δ, ppm: 7.12 (s, 2H, Ar-H), 3.35 (s, 2H, CH). ¹³C NMR (CDCl₃), δ, ppm: 132.6, 123.6, 100.4, 82.2.

2,5-bis1-(3,4,5-tris(Decyloxy)phenyl)-1H-1,2,3-triazol-4-yl)thiophene (11a). The mixture of 0.22 g (1.7 mmol) of compound 10, 0.032 g (0.17 mmol) of CuI, 20 mL of solution ethanol/H₂O (1/1) three drops of Et₃N were added and stirred for 20 m. After that, 2.2 g (3.7 mmol) of compound 6a was added drop wise and stirred at 50°C for 24 h. Then 40 mL of H₂O was added in the mixture and the solid was filtered off. The purification was by column chromatography on silica, hexane/AcOEt (95/5) as eluent, obtained 1.5 g of yellow solid (54%). IR (KBr pellet) ν_{max} cm⁻¹: 3124, 2954, 2924, 2851, 1600. ¹H NMR (400 MHz, CDCl₃), δ, ppm: 8.06 (s, 2H, Ar-H), 7.46 (s, 2H, Ar-H), 6.94 (s, 4H, Ar-H), 4.04 (m, 8H, –OCH₂), 4.00 (m, 4H, –OCH₂) 1.84 (m, 12H, –CH₂), 1.77 (m, 6H, –CH₂), 1.49 (m, 12H, –CH₂), 1.28 (m, 66H, –CH₃), 0.88 (m, 18H, –CH₃). ¹³C NMR (CDCl₃), δ, ppm: 153.8, 142.9, 138.6, 132.3, 132.2, 125.0, 117.5, 99.6, 73.7, 69.5, 31.9, 29.3, 26.0, 22.7, 14.1. Calcd: m/z 1308.0138 (M + H⁺). Found: m/z 1308.0138 (M + H⁺), 100%.
2H, Ar-H), 4.08 (t, J = 6.6 Hz, 4H, -OCH2), 4.05 (t, J = 6.6 Hz, 4H, -OCH2), 1.85 (m, 8H, -CH2), 1.49 (m, 8H, -CH2), 1.28 (m, 48H, -CH2), 0.88 (m, 12H, -CH3). Calcd: m/z 959.7130 [(M + H)+]. Found: Q-TOF/MS m/z 959.7141 [(M + H)+, 100%].

2,5-bis(1-(4-(Decyloxy)phenyl)-1H-1,2,3-triazol-4-yl) thiophene (11c). It was prepared according to the procedure written for compound 11a. The purification was through recrystallisation in THF, affording 1.2 g of yellow solid (48%). IR (KBr pellet) νmax cm⁻¹: 3126, 2953, 2920, 2850, 1519. ¹H NMR (400 MHz, CDCl3), δ, ppm: 8.04 (s, 2H, Ar-H), 7.67 (d, J = 8.8 Hz, 4H, Ar-H), 7.48 (s, 2H, Ar-H), 7.05 (d, J = 8.8 Hz, 4H, Ar-H), 4.03 (t, J = 6.6Hz, 4H, -OCH2), 1.83 (m, 4H, -CH2), 1.29 (m, 28H, -CH2), 0.89 (m, 6H, -CH3). Calcd: m/z 683.4012 [(M + H)+, 100%]. Found: Q-TOF/MS m/z 683.4102 [(M + H)+, 100%].

Synthesis of asymmetrical compounds

2-(4-(Decyloxy)phenyl)ethynyl)-5-iodothiophene (13). The mixture of 3.48 g (10.3 mmol) of compound 12 was dissolved in 10 mL of triethylamine and the solvent removed in rotary evaporation. The purification was through column chromatography on silica, hexane as eluent, affording 1.0 g of yellow solid (74%). Mp: 47–55°C.

4-(5-((4-(Decyloxy)phenyl)ethynyl)thiophen-2-yl)-1-(3,4-tris((decyloxy)phenyl)-1H-1,2,3-triazole (15). Firstly, 1.57 g (3.7 mmol) of compound 14, 0.14 g (0.37 mmol) of NaOH on 80 mL of toluene, refluxed for 4 h. The mixture was filtered and the solvent removed in rotary evaporation. The purification was through column chromatography on silica, hexane as eluent, affording 1.0 g of yellow solid (74%). Mp: 47–55°C.

4-(5-((3,4-bis((decyloxy)phenyl)ethynyl)thiophen-2-yl)-1-(3,4-tris((decyloxy)phenyl)-1H-1,2,3-triazole (16a). The mixture of 0.25 g (0.68 mmol) of compound 15, 0.07 g (0.068 mmol) of CuI on 20 mL of ethanol/H2O 1/1 and three drops of Et3N, was stirred for 20 m. After that, 0.52 g (0.89 mmol) of compound 16a was added drop wise and stirred at 50°C for 24 h. The mixture was poured in 40 mL of H2O, the solid filtered off. The purification was through column chromatography on silica, hexane/AcEt (97:3) as eluent, affording 0.30 g of yellow solid (46%). Mp: 77–80°C.

4-(5-((3,4-bis((decyloxy)phenyl)ethynyl)thiophen-2-yl)-2-methylbut-3-yn-2-ol (14). It was prepared according to the procedure written for compound 13. The purification was through column chromatography on silica, hexane/AcEt (95/5) as eluent, affording 4.2 g of yellow solid (59%). Mp: 73–76°C.
compound 16a. The purification was through recrystal-
lation in hexane, affording 0.35 g of yellow solid (52%). Mp: 124°C. IR (KBr pellet) νmax cm⁻¹: 3130, 2954, 2918, 2850, 1604. ¹H NMR (400 MHz, CDCl₃), δ ppm: 8.01 (s, 1H, Ar-H), 7.74 (d, J = 8.3 Hz, 2H, Ar-H), 7.35 (d, J = 3.9 Hz, 1H, Ar-H), 7.34 (d, J = 2.3 Hz, 1H, Ar-H), 7.22 (d, J = 3.9 Hz, 1H, Ar-H), 7.17 (dd, J = 8.6 Hz, 1H, Ar-H), 6.97 (d, J = 8.6 Hz, 1H, Ar-H), 6.88 (d, J = 8.6 Hz, 2H, Ar-H), 4.07–4.04 (m, 4H, -OCH₂), 3.97 (t, J = 6.6 Hz, 2H, -OCH₂), 1.84–1.78 (m, 6H, -CH₂), 1.47 (m, 6H, -CH₂), 1.27 (m, 36H, -CH₂), 0.88 (m, 9H, -CH₃), ¹³C NMR (CDCl₃), δ ppm: 164.3, 159.8, 150.2, 149.9, 143.0, 133.8, 133.2, 132.4, 130.6, 124.5, 123.8, 117.9, 114.9, 113.9, 112.9, 107.1, 94.7, 81.3, 69.9, 68.4, 32.2, 29.9, 28.9, 29.7, 29.5, 26.3, 23.0, 14.4. Caled: m/z 796.5455 [(M + H)+, 100%].

1-(4-(Decyloxy)phenyl)-4-(5-((4-(decyloxy)phenyl)ethylthiophen-2-yl)-1H-1,2,3-triazole (16c). It was prepared according to the procedure written for compound 16a. The purification was through maceration in hot hexane, affording 0.40 g of yellow solid (76%). IR (KBr pellet) νmax cm⁻¹: 3128, 2953, 2920, 2850, 1604. ¹H NMR (400 MHz, CDCl₃), δ ppm: 8.01 (s, 1H, Ar-H), 7.66 (d, J = 8.9 Hz, 2H, Ar-H), 7.46 (d, J = 8.8 Hz, 2H, Ar-H), 7.35 (d, J = 3.5 Hz, 1H, Ar-H), 7.22 (dd, J = 3.5 Hz, 1H, Ar-H), 7.03 (d, J = 8.9Hz, 2H, Ar-H), 6.88 (d, J = 8.8 Hz, 2H, Ar-H), 4.01 (t, J = 6.6 Hz, 2H, -OCH₂), 3.97 (t, J = 6.6Hz, 2H, -OCH₂), 1.80 (m, 4H, -CH₂), 1.45 (m, 4H, -CH₂), 1.28 (m, 24H, -CH₂), 0.88 (t, J = 6.8 Hz, 6H, -CH₃), ¹³C NMR (CDCl₃), δ ppm: 159.6, 159.4, 146.9, 142.8, 133.4, 132.9, 132.1, 130.0, 124.2, 123.5, 122.2, 117.5, 115.3, 114.6, 94.3, 81.1, 68.5, 68.1, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 25.4, 22.7, 14.1. Caled: m/z 640.3926 (M + H)+. Found: Q-TOF/MS m/z 640.3931 [(M + H)+, 100%].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

Supplemental data for this article can be accessed here.

References

[1] Nam S, Shin M, Park S, et al. All-polymer solar cells with bulk heterojunction nanolayers of chemically doped electron-donating and electron-accepting polymers. Phys Chem Chem Phys. 2012;14:15046–15053. DOI:10.1039/c2cp43002a.

[2] Yohsuke B, Urayama K, Takigawa T, et al. Biaxial strain testing of extremely soft polymer gels. Soft Matter. 2011;7:2632–2638. DOI:10.1039/c0sm00955e.

[3] Kawabata K, Takeguichi M, Goto H. Optical activity of heteroaromatic conjugated polymer films prepared by asymmetric electrochemical polymerization in cholesteric liquid crystals: structural function for chiral induction. Macromolecules. 2013;46:2078–2091. DOI:10.1021/ma400302j.

[4] Jia X-X, Li Z-W, Sun Z-Y, et al. Hierarchical self-assembly of soft disclike particles under shear flow. J Phys Chem B. 2011;115:13441–13448. DOI:10.1021/ jp205683x.

[5] Tabor RF, Zaveer MI, Dagastine RR, et al. Phase behavior, small-angle neutron scattering and rheology of ternary nonionic surfactant-oil-water systems: a comparison of oils. Langmuir. 2013;29:3575–3582. DOI:10.1021/la400100m.

[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. 2013;178:222–227. DOI:10.1016/j.snb.2012.12.036.

[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. 2013;132:13654–13656. DOI:10.1021/ja406220j.

[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] Bisoyi HK, Kumar S. Liquid-crystal nanoscience: an emerging avenue of soft self-assembly. Chem Soc Rev. 2011;40:306–319. DOI:10.1039/B901793N.

[11] Shanavas A, Sathiyaraj S, Chandramohan A, et al. Isophthalic acid based mesogenic dimers: synthesis and structural effects on mesophase properties. J Mol Struct. 2013;1038:126–133. DOI:10.1016/j.molstruc.2013.01.047.

[12] McKenzie I, Cammidge AN, Gopee H, et al. Muoniated spin probes in the discotic liquid crystal HHTT: rapid electron spin relaxation in the hexagonal columnar and isotropic phases. Phys Rev E. 2013;87:012504/1–012504/8. DOI:10.1103/PhysRevE.87.012504.

[13] Cristiano R, Santos DMPDO, Conte G, et al. 1,4-diaryl and Schiff’s base [1,2,3]-triazole derivative liquid crystalline compounds. Liq Cryst. 2006;33:997–1003. DOI:10.1080/02678290600916138.
E. Giroto et al.

[14] Vasconcelos UB, Merlo AA. Synthesis and mesomorphic behavior of new n-heterotolane liquid crystals containing a naphthyl-pyridyl framework. Synthesis. 2006;7:1141–1147.

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

[16] Hashim Z, Howes P, Green M. Luminescent quantum-dot-sized conjugated polymer nanoparticles: nanoparticle formation in a miniemulsion system. J Mater Chem. 2011;21:1797–1803. DOI:10.1039/C0JM02935A.

[17] Maggini L, Bonifazi D. Hierarchised luminescent architectures: design, synthesis, self-assembly, self-organisation and functions. Chem Soc Rev. 2012;41:211–241. DOI:10.1039/C1CS15031F.

[18] Wang H, Xu Y, Tsuboi T, et al. Energy transfer in polyfluorene copolymer used for white-light organic light emitting device. Org Electron. 2013;14:827–838. DOI:10.1016/j.orgel.2012.12.039.

[19] Behramand B, Molin F, Gallardo H, et al. 2,1,3-Benzoxadiazole and 2,1,3-benzothiadiazole-based fluorescent compounds: synthesis, characterization and photophysical/electrochemical properties. Dyes Pigm. 2012;95:600–605. DOI:10.1016/j.dyepig.2012.06.001.

[20] Prabhu DD, Kumar NSS, Sivadas AP, et al. Trigonal 1,3,4-oxadiazole-based blue emitting liquid crystals and gels. J Phys Chem B. 2012;116:13071–13080. DOI:10.1021/jp305349h.

[21] Yuan K, Li F, Chen L, et al. Liquid crystal helps ZnO nanoparticles self-assemble for performance improvement of hybrid solar cells. J Phys Chem C. 2012;116:6332–6339. DOI:10.1021/jp3004079.

[22] Fujisaki Y, Nakajima Y, Takei T, et al. Flexible active-matrix organic light-emitting diode display using air-stable organic semiconductor of dinaphtho[2, 3-b:2’, 3’-f]thieno[3, 2-b]thiophene [2, 3-h]. IEEE Trans Electron Devices. 2012;59:3442–3449. DOI:10.1109/TED.2012.2220968.

[23] Vieira AA, Gallardo H, Barberá J, et al. Luminescent columnar liquid crystals generated by self-assembly of 1,3,4-oxadiazole derivatives. J Mater Chem. 2011;21:5916–5922. DOI:10.1039/c0jm04570e.

[24] Chen X, Li X, Yuan J, et al. Simple, efficient one-pot method for synthesis of novel N-attached 1,2,3-triazole containing bisphosphonates. Tetrahedron. 2013;69:4047–4052. DOI:10.1016/j.tet.2013.03.078.

[25] Glowacka IE, Balzarini J, Wroblewski AE. Synthesis and biological evaluation of novel 1,2,3-triazolonucleotides. Arch Pharm. 2013;346:278–291. DOI:10.1002/ardp.201200421.

[26] Gallardo H, Bortoluzzi AJ, Santos DMPDO. Synthesis, crystalline structure and mesomorphic properties of new liquid crystalline 1,2,3-triazole derivatives. Liq Cryst. 2008;35:719–725. DOI:10.1080/0267829080120307.

[27] Bergthaller P. A new method for the synthesis of two-equivalent couplers in colour photography. Sulfur Rep. 1996;18:337–356. DOI:10.1080/1961779608047899.

[28] Benbayer C, Kheddam N, Saidi-Besbes S, et al. Synthesis and mesomorphic properties of novel [1,2,3]-triazole mesogenic based compounds. J Mol Struct. 2013;1034:22–28. DOI:10.1016/j.molstruc.2012.09.020.

[29] Balamurugan S, Yeap G-Y, Mahmoud WAK. Calixarene liquid crystals of 1,2,3-triazole connected to azobenzene: synthesis, characterisation and anisotropic properties. Liq Cryst. 2014;41:776–783. DOI:10.1080/02678292.2014.899231.

[30] Westphal E, Bechthold IH, Gallardo H. Synthesis and optical/thermal behavior of new azo photosomerizable discotic liquid crystals. Macromolecules. 2010;43:1319–1328. DOI:10.1021/ma902460c.

[31] Heng B-T, Yeap G-Y, Mahmoud WAK, et al. New heterocyclic metallomesogens: synthesis, mesomorphic and thermal behaviours of Cu(II) complexes with 1,2,3-triazole-based Schiff bases ligands. Liq Cryst. 2015;42:204–215. DOI:10.1080/02678292.2014.975291.

[32] Heng B-T, Yeap G-Y, Mahmoud WAK, et al. Alkyl chain self-ordering, induction and suppression of mesophase by Cu(II) containing [1,2,3]-triazole-based bidentate salicylaldimine ligands: synthesis, characterisation and X-ray diffraction studies. Liq Cryst. 2014;41:1897–1910. DOI:10.1080/02678292.2014.960488.

[33] 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.

[34] Umesh CP, Gangarapu S, Marcelis ATM, et al. Discotic liquid crystalline tris(hexaheloyxtriphenylene)triazines with separate columns of triphenylene and triazine cores. Liq Cryst. 2014;41:1862–1872. DOI:10.1080/02678292.2014.956353.

[35] 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.

[36] Giroto 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.

[37] Laurent N, LaFont D, Dumoulin F, et al. Synthesis of amiphilic phenylazophenyl glycosides and a study of their liquid crystal properties. J Am Chem Soc. 2003;125:15499–15506. DOI:10.1021/ja037347x.

[38] Seidler A, Svoboda J, Dekoj V, et al. The synthesis of 3-electron molecular rods with a thiophene or thieno[3,2-b]thiophene core unit and sulfur alligator clips. Tetrahedron Lett. 2013;54(22):2795–2798. DOI:10.1016/j.tetlet.2013.03.084.

[39] Gallardo H, Ely F, Bortoluzzi A, et al. Applying click chemistry to synthesis of chiral [1,2,3]-triazole liquid crystals. Liq Cryst. 2005;32:667–671. DOI:10.1080/02678290500139732.

[40] Zhang ZL, Zhang LY, Shen ZH, et al. Synthesis and properties of mesogen-jacketed liquid crystalline polymers containing bisthiole mesogen. J Polym Sci Part A: Polym Chem. 2010;48:4627–4639. DOI:10.1002/pola.v48.21.

[41] Han J, 1,3,4-oxadiazole based liquid crystals. J Mater Chem C. 2013;1:7779–7797. DOI:10.1039/c3tc31458h.
[42] Goodby JW, Mandle RJ, Davis EJ, et al. What makes a liquid crystal? The effect of free volume on soft matter. Liq Cryst. 2015;42:593–622.

[43] Kishikawa K, Aikyo S, Akiyama S, et al. Realization of a lateral directional order in nematic and smectic A phases of rodlike molecules by using perfluoroarene–arene interactions. Soft Matter. 2011;7:5176–5187. DOI: 10.1039/c0sm01459a.

[44] 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.

[45] 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 Mater Chem C. 2013;1:7488–7497. DOI:10.1039/c3tc31724b.

[46] 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 Mater Chem. 2008;18:3954–3964. DOI:10.1039/b804189j.

[47] Tang J, Huang R, Gao H, et al. Columnar mesophases of luminescent polycatenar liquid crystals incorporating a 1,3-substituted benzene ring interconnecting two 1,3,4-oxadiazoles. RSC Adv. 2012;2:2842–2847. DOI:10.1039/c2ra01362b.