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 , Ely, Fernando and Gallardo, Hugo(2005) 'Light-emitting bent-shape liquid crystals', Liquid Crystals, 32: 1, 15 — 25
To link to this Article: DOI: 10.1080/02678290412331329279
URL: http://dx.doi.org/10.1080/02678290412331329279

Liquid Crystals, Vol. 32, No. 1, January 2005, 15–25

Taylor & Francis
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Light-emitting bent-shape liquid crystals

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(*Received 20 June 2004; accepted 29 September 2004*)

Symmetric and asymmetric bent-shape LCs were synthesized, having the emissive core 1,3,4-oxadiazole with C≡C bonds as connecting groups, and terminal nitro lateral substituents. Thermal behaviour was determined using optical microscopy and differential scanning calorimetry. Lowering of transition temperatures and/or induction of new smectic phases in the symmetric compounds was observed on the introduction of terminal polar nitro groups, as compared with unsubstituted symmetric compounds. The observed LC phases possess the classical textures of calamitic liquid crystals and no B-phases were found, despite the fact that the bending angle of the oxadiazole ring (134°) should be large enough to give polar packing. Luminescent properties, in solution, of the final compounds were evaluated and a strong blue fluorescence was observed from 390 to 410 nm with good photoluminescence quantum yields (71–84%) for compounds without the nitro substituent. The introduction of a nitro group at the external rings of the molecules led to a very strong reduction in the emissive properties, which is attributed to $n \rightarrow \pi^*$ excitation of this group.

1. Introduction

When Helfrich observed a glowing blue colour on passing an electric current through anthracene crystals he would never have imagined using such emissions of visible light in display devices [1–3]. However, in recent years considerable effort has been dedicated to the development of electroluminescent polymers [4, 5] and small molecules [6, 7] for use in what are now called organic light-emitting diodes (OLEDs). Among the advantages of OLEDs over inorganic LEDs are their light weight, large active area and flexibility. In addition to polymers and low-molar-mass materials, highly conjugated liquid crystalline compounds have also emerged as good alternatives for OLEDs [8–15]. LCs are typical self-organizing materials with unique properties. For example, the self-organized structures are controlled by the choice of phases of LC materials, so that structurally controlled thin films can be prepared by quenching from appropriate fluid phases into solid states [16]. Furthermore, LCs possess high carrier-transport ability, are able to achieve linearly polarized electroluminescence (EL) and defect-free layers. These liquid crystalline properties are promising for introducing new features into conventional organic LEDs. For example, Contoret *et al.*[17] have reported polarized electroluminescence from a nematic network that can be a substitute for one of the polarizers and the back light of TN-LCDs and STN-LCDs, with a lower power consumption and/or a higher brightness. LCs have also shown large hole/electron mobilities, another important aspect in OLEDs, in discotic hexagonal (Col_h), helical (H) and smectics A, B and an undentified X phase [18–22]. In this context we have considered the design, synthesis and characterization of new light-emitting liquid crystals possessing bent shape (figure 1).

The target compounds **1**–**6** bear in the molecular structure the 1,3,4-oxadiazole ring, a recognized blue emitter and electron-transporting moiety, and triple bond(s) as the connecting group(s) between phenyl rings. Bent-shape mesogens possessing a large dipole moment from the oxadiazole ring and/or nitro groups might be expected to display polar phases due to the combination of dipolar forces and packing considerations arising from the shape anisotropy of the molecules. As a result highly ordered materials may be obtained with good charge transport and emissive capabilities.

2. Results and discussion

2.1. *Design*

The target compounds were designed with the consideration of their geometric and electronic aspects. The desired bent shape was achieved either by introducing

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331329279

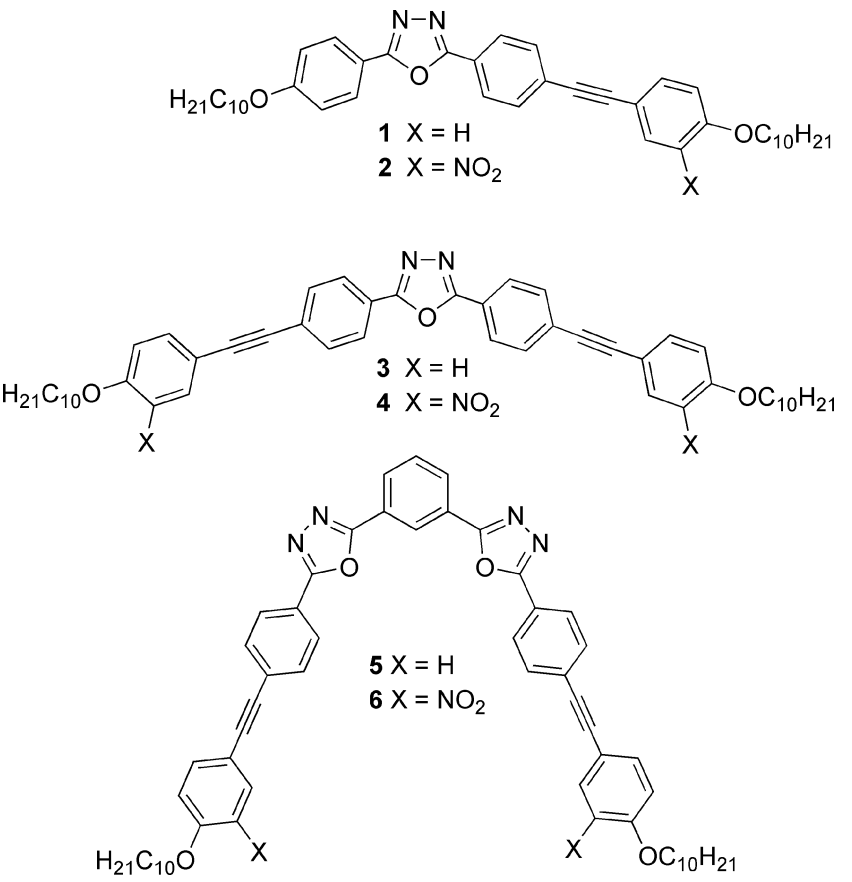


Figure 1. Liquid crystals containing the oxadiazole ring with bent shape.

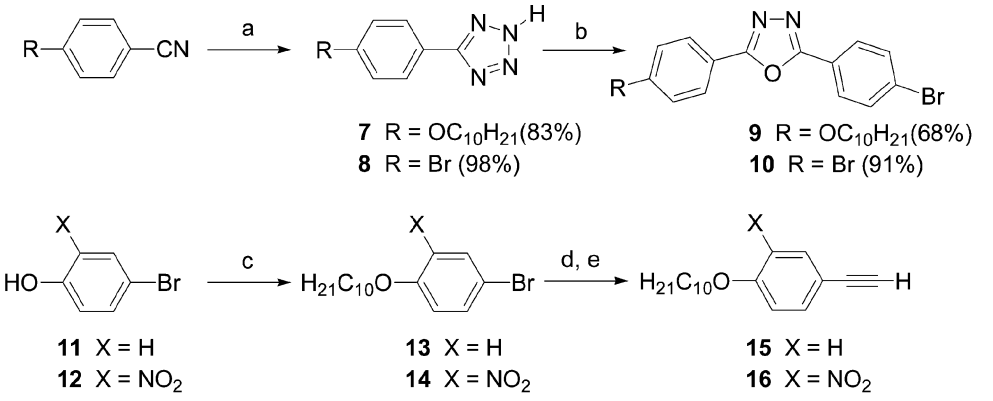
the 2,5-disubstituted heterocycle 1,3,4-oxadiazole (compounds **1**–**4**) or by using the 1,3-phenylene central unit (compounds **5** and **6**). Specifically, compounds **3**–**6**, according to Weissflog [23], can be classified as banana mesogens because they contain five and seven aromatic rings and bending angles that produce strongly non-linear structures. Banana liquid crystalline phases have received much attention in recent years and novel ferroelectric and antiferroelectric mesophases were obtained from initially achiral molecules [24–33]. Triple C≡C bonds were used as linking groups in order to produce the highly π-polarizable and conjugated tolane moiety. Diphenylacetylenes or tolanes are very interesting materials for reasons such as their large birefringence [34–36], large index of refraction parallel to the director, large electric polarizability and the ability to form optical films transparent in the visible. Another important factor is the presence of lateral dipoles related to mesomorphic behaviour. The influence on mesomorphic properties of a lateral substituent attached to terminal phenyl rings has been less studied [37, 38] than the effect of substituents in the central unit in banana mesogens.

2.2. *Synthesis*

The syntheses of oxadiazole ring derivatives and terminal aryl acetylenes were carried out according to scheme 1. Treatment of the respective aryl nitriles with NaN_3/NH_4Cl in DMF at about 100°C led to tetrazoles **7** and **8**, which were reacted with 4-bromobenzoyl chloride under refluxing pyridine (Huisgen reaction) to give the 1,3,4-oxadiazoles **9** and **10** in 66% and 91% yields, respectively. The terminal aryl acetylenes were synthesized starting from compounds **11** and **12** by the sequence alkylation, palladium catalysed cross coupling (Sonogashira coupling) [39] with the commercially available 2-methyl-3-butyn-2-ol, and protective group elimination to afford the desired compounds **15** and **16**.

Scheme 2 indicates the synthetic route to the target compounds **1**–**4** by palladium-catalysed coupling between aryl halides and terminal aryl acetylenes.

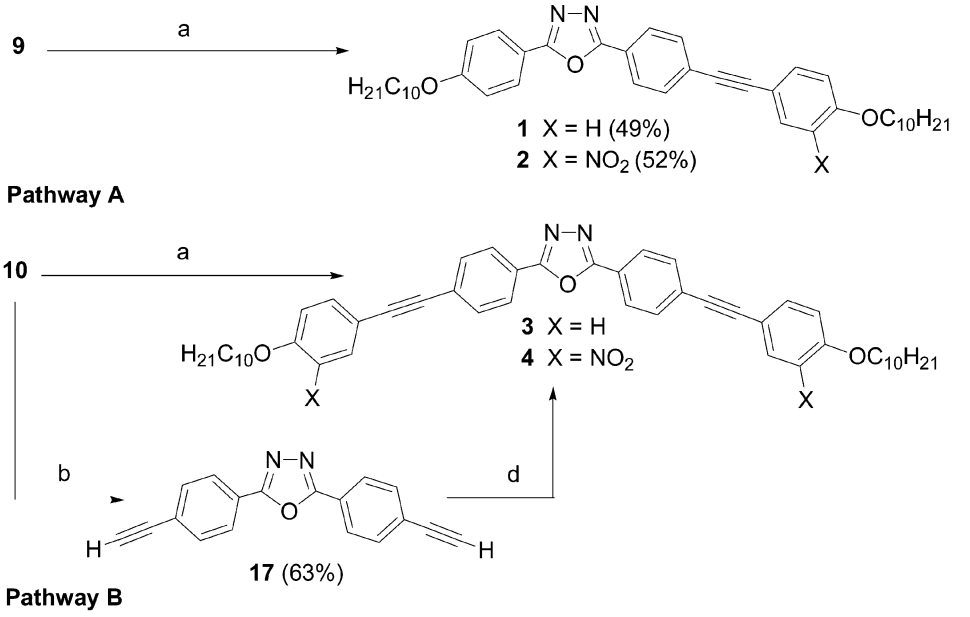
Compounds **1** and **2** were obtained from **9** in 49% and 52% yields, respectively. For the synthesis of the symmetric compounds **3** and **4** pathway A was initially employed but resulted in low yields (42% of **4** and only traces of **3**) with a considerable amount of homocoupling product **20**; see table 1 and figure 2. The synthesis



Reagents: a. NaN_3, NH_4Cl, DMF, 100ºC; b. *p*-bromobenzoyl chloride, pyridine reflux; c. *n*-decylbromide, K_2CO_3, butanone, reflux; d. 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; e. NaOH, toluene, reflux.

Scheme 1. Synthesis of the intermediate aryl bromides and terminal aryl acetylenes. Reagents: a. NaN_3, NH_4Cl, DMF, 100°C; b. *p*-bromobenzoyl chloride, pyridine reflux; c. *n*-decylbromide, K_2CO_3, butanone, reflux; d. 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; e. NaOH, toluene, reflux.

was optimized by simply reversing the functionalities according to pathway B. Starting from **10**, the terminal aryl diacetylene **17** was prepared in 63% overall yield. Pathway B was successfully completed with a second palladium cross-coupling furnishing **3** (35% yield) and **4** (53% yield).



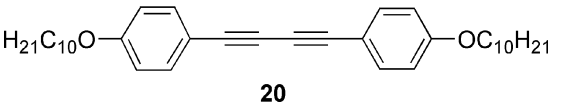
Reagents: a. **15** or **16**, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; b. i) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; ii) NaOH, toluene, reflux; d. *p*-iodophenol, $PdCl_2(PPh_3)_2$, CuI, TEA/THF, rt (compound **3**) or aryl bromide **14**, $PdCl_2(PPh_3)_2$, CuI, TEA reflux (compound **4**).

Scheme 2. Synthesis of the final compounds **1**–**4**. Reagents: a. **15** or **16**, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; b. i) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, TEA, reflux; ii) NaOH, toluene, reflux; d. *p*-iodophenol, $PdCl_2(PPh_3)_2$, CuI, TEA/THF, rt (compound **3**) or aryl bromide **14**, $PdCl_2(PPh_3)_2$, CuI, TEA reflux (compound **4**).

Table 1. Results of the palladium cross-coupling for compounds **3** and **4**.

Compound	*X*	Pathway	Yield/%
3	H	A	—
3	H	B	35
4	NO_2	A	42
4	NO_2	B	53

The series based on the 1,3-substituted benzene core (banana shape) was synthesized according to scheme 3. Isophthaloyl chloride, previously prepared from isophthalic acid under reflux in $SOCl_2$ for 12 h, was reacted with aryl tetrazole **8** to give the 1,3,4-oxadiazole ring **18** in 92% yield, followed by palladium cross-coupling with 2-methyl-3-butyn-2ol and deprotection to furnish terminal aryl diacetylene **19** in 56% overall yield. Finally, the same conditions used to obtain **3** and **4** were employed to give **5** and **6** in 21% and 16% yield, respectively, after several recrystallizations.

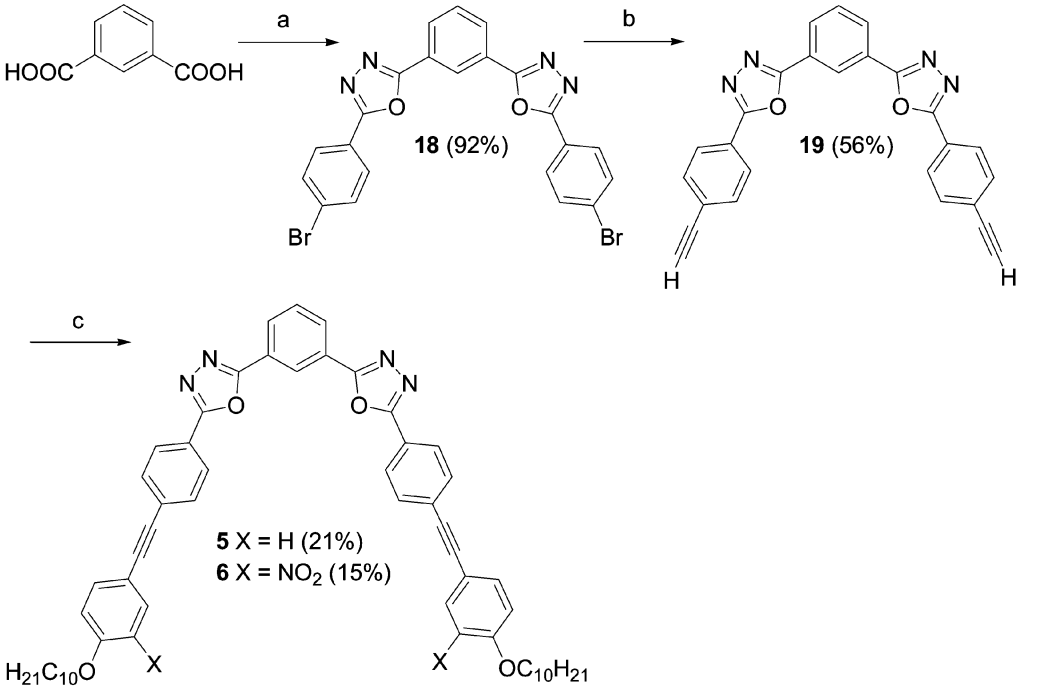


20

Figure 2. Homocoupling product.

2.3. *Liquid crystalline profile of the final compounds*

The transition temperatures, phase assignments and thermal stability of the final compounds were investigated by thermal polarizing optical microscopy (POM), DSC and TGA and results are presented in table 2. All the compounds exhibited high thermal stability. Compounds **1**–**4**, with moderate bending angles, (theoretically about 134°) [40] show smectic and nematic phases that are typical for calamitic liquid crystals. Despite compound **1** possessing a monotropic smectic transition at 128.5°C, the compounds without terminal lateral nitro substituents exhibited, essentially, nematic phases with typical schlieren texture, figure 3 (*a*). On the other hand, compounds bearing terminal nitro group substituents showed smectic C and A phases over wider



Reagents: a. aryl tetrazole **8**, pyridine, reflux; b. i) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, DMA, 115ºC; ii) NaOH, toluene, reflux; d. 4-*n*-decyloxyiodophenol, $PdCl_2(PPh_3)_2$, CuI, TEA/THF, rt (compound **5**) or aryl bromide **14**, $PdCl_2(PPh_3)_2$, CuI, TEA, reflux (compound **6**).

Scheme 3. Synthesis of the final compounds **5** and **6**. Reagents: a. aryl tetrazole **8**, pyridine, reflux; b. i) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, TPP, DMA, 115°C; ii) NaOH, toluene, reflux; d. 4-*n*-decyloxyiodophenol, $PdCl_2(PPh_3)_2$, CuI, TEA/THF, rt (compound **5**) or aryl bromide **14**, $PdCl_2(PPh_3)_2$, CuI, TEA, reflux (compound **6**).

Table 2. Thermal behaviour of compounds **1**–**6**.

Compound	Transition	T/°C, heating (ΔH/kJ mol^{-1})[a]	T/°C, cooling (ΔH/kJ mol^{-1})[a]	$T_{dec.}$/°C[b]
1	CrI–CrII	116.1 (7.92)	105.0 (−7.44)	438
	CrII–(SmC)		125.8 (−19.3)	
	(SmC)–N	131.6 (23.1)	128.4 (−0.29)	
	N–I	156.3 (0.67)	152.2 (−0.66)	
2	CrI–CrII	60.2 (21.4)	57.1 (−32.2)	353
	CrII–SmC	126.5 (22.3)	111.2 (−24.4)	
	SmC–SmA	152.6 (broad)	150.9 (broad)	
	SmA–I	161.9 (3.58)	152.6 (−2.93)	
3	Cr–N	212.5 (51.8)	197.4 (−50.9)	350
	N–I	234.8 (0.79)	232.5 (broad)	
4	Cr–SmC	119.9 (18.4)	<25.0	322
	SmC–SmA	146.6 (8.58)	138.7 (−8.49)	
	SmA–I	230.2 (2.31)	222.3 (−2.12)	
5	Cr–SmX[c]	258.5 (29.6)	248.3 (−27.1)	300
	SmX–I	294.9 (broad)		
6	Cr–SmX	220.5 (23.1)	204.7 (−8.7)	250
	SmX–I	250.0 (broad)		

[a]Determined by optical microscopy and DSC measures (5°C min^{-1}). [b]Determined by TGA, onset of decomposition in nitrogen, 10°C min^{-1}. [c]SmX=smectic mesophase not classified.

temperature ranges and with lower melting points. Typical textures observed for **2** and **4** are shown in figures 3(*b*) and 3(*c*), respectively. The thermal behaviour of compounds **5** and **6**, containing seven aromatic rings and considerable bending angles, was determined up to 300 and 250°C, respectively. Above these temperatures, thermal decomposition was observed.

The symmetric mesogens possess average C_{2V} symmetry, which could lead to optical biaxiality in the SmA phase. For this reason, conoscopic experiments were carried out on **4**, **5** and **6**. However, all attempts to obtain sufficiently aligned monodomains were unsuccessful due to the high transition temperatures that lead to substantial decomposition.

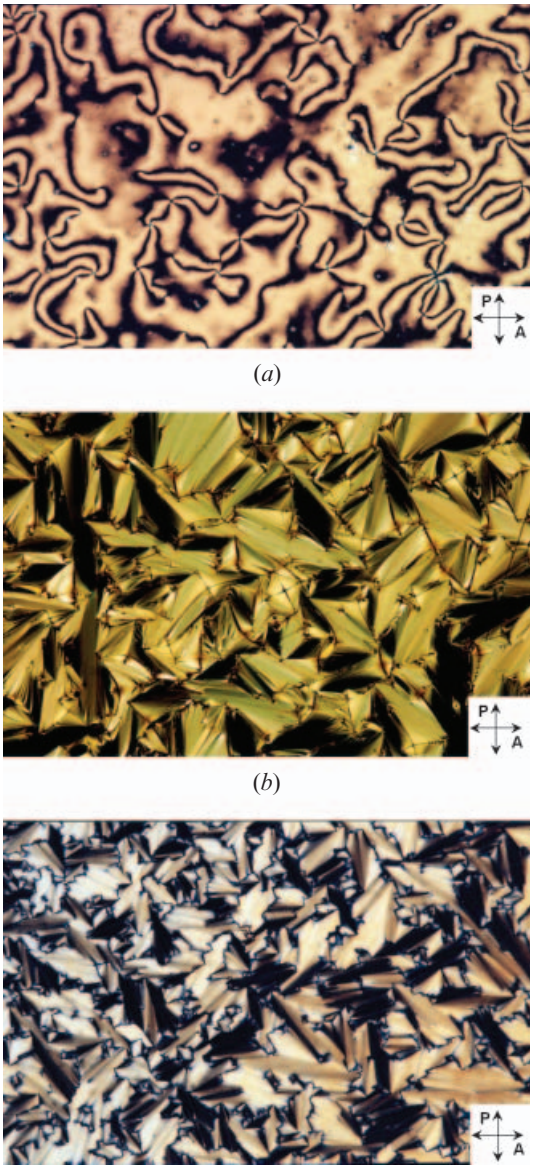
Samulski *et al.*[40] working with low-molar-mass liquid crystals based on the oxadiazole ring have found the existence of two optical axes in the SmA phase, although they were unable to discern between the 'McMillan' and the ferroelectric arrangement of the bent mesogens. On the other hand, the same authors prepared similar compounds by changing only the directional sense of the ester linkage and obtained a rich and complex polymorphism where no consistent evidence of biaxility was obtained [41]. Further, Madsen and colleagues investigating those compounds, identified biaxiality for the nematic phase by performing NMR experiments using a deuterated mesogen [42]. This identification is consistent with X-ray studies by Acharya *et al.*[43], in which the minor director was aligned by applying an electric field. The reason for the substitution of the central ring by a five-membered heterocycle to result in nematic or smectic mesophases typical for calamitic liquid crystals is still not clear. After all, the bending angle imposed by the heterocycle ring should be sufficient to give a polar packing which would form B-phases [23]. However, not only geometric factors seem to be operating in this type of bent-core LCs containing a five-membered heterocyclic central or lateral ring. Strong electrostatic forces have been suggested as crucial in stabilizing the biaxial nematic for these materials. The large electric dipole moment of the oxadiazole would result a strong intermolecular association that reinforces transverse orientational correlations [42]. In that context one expected result could be a nematic phase with ferroelectric properties. Indeed, Torgova *et al.* have found values of $\mathbf{P}_S$ from 200 to 300 nC cm^{-2}, in both smectic and nematic, for related compounds based on the 1,2,4-oxadiazole ring [44].

2.4. *UV-Vis absorption and photoluminescence spectroscopy*

The photophysical data for final compounds **1**–**6** are shown in table 3. The photoluminescence quantum yield, Φ_{PL}, was calculated according to equation (1).

$$_{PL} = _{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2 \qquad (1)$$

where Φ_{std} is the photoluminescence quantum yield of the standard quinine sulphate (Φ_{std}=0.546; 1N H_2SO_4); I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively; A_{unk} and A_{std} are the absorbance of the sample and standard, respectively, at the desired wavelength λ_{exc} (340 nm); and η_{unk}



(*a*)

(*b*)

(*c*)

Figure 3. Photomicrographs of (*a*) the N phase schilieren texture at 144.2°C for compound **1** (66×); (*b*) SmA phase focal-conic texture at 187.0°C for compound **4** (33×); and (*c*) SmC phase broken fan-shaped texture at 133.0°C for compound **4** (33×). Samples were sandwiched between untreated glass slides and viewed through crossed polarizers.

and η_{std} are the refractive indexes of the sample and standard solutions.

Excitation and photoluminescence spectra of **1**, **3** and **5** in chloroform solution exhibit an intense absorption band peaking between 330 and 350 nm with high molar absorptivity and an intense blue emission (λ_{em}=390–410 nm) with good photoluminescence quantum yields (80, 84 and 71% respectively); see figure 4 and table 3. Compound **3** gave a structured photoluminescence spectrum with two emission peaks; the Stokes shift lies between 60 and 70 nm, and the luminescence lifetime decay is 0.7–0.9 ns. Based on emission energy, lifetimes and quantum yields, the luminescence of **1**, **3** and **5** is attributed to π–π^* fluorescence in all cases. The emission anisotropy, $<r>$, was evaluated using equation (2),

$$\langle r\rangle = (I_V - I_H)/(I_V + 2I_H) \qquad (2)$$

where I_V and I_H are the vertical and horizontal polarized fluorescence intensity, respectively. Low values were found (table 2) for all compounds, indicating reduced polarization and high mobility of the molecules in solution. The nitro derivatives **2**, **4** and **6** presented weak blue fluorescence and poor quantum yields. On analysing their molecular structure one can see that they are non-resonant in the classical sense since the 'donor' group (triple bond) is *meta* to the acceptor (nitro) [45]. Although the presence of strong lateral dipoles is valuable for increasing dipolar interactions in the liquid crystalline phase, the diminished resonance is detrimental to emissive properties. However, the weak fluorescence from nitro derivatives may be attributed mainly to excitation $n\rightarrow\pi^*$ from the nitro group that suppresses the $\pi\rightarrow\pi^*$ from the conjugated aromatic rings [46]. Figure 5 shows fluorescence spectra of compounds **1** and **2** under the same experimental conditions. Derivative **1** presents strong emission peaking at 395 nm with a very good quantum yield of 80%; the similar compound **2** bearing the nitro group emits almost no light.

3. Conclusions

A new class of liquid crystals, containing the oxadiazole ring, carbon–carbon triple bonds as connecting groups, and a nitro lateral substituent has been synthesized. The effect of the presence of terminal nitro lateral substituents was evaluated. The bent-shape liquid crystals showed nematic, smectic A, C and an additional smectic X (not identified) phase. The LC phases have classical textures of calamitic liquid crystals and there was no evidence for B-phases. High transition temperatures prohibited conoscopic studies for biaxility verification, because during the experiments strong decomposition took place. Luminescence properties of the final compounds were also evaluated. Strong blue fluorescence was verified from 390 to 410 nm with good photoluminescence quantum yields of 71–84% for compounds with no terminal nitro lateral substituent. The introduction of a nitro group at the terminal rings of the bent-shape molecules led to a very strong reduction in emissive properties, attributed to the excitation $n\rightarrow\pi^*$ of the nitro group. Efforts to

Table 3. Photophysical properties of compounds **1**–**6**, measured in chloroform solution.

Compound	$\lambda_{abs.}$/nm (ε)[a]	$\lambda_{em.}$/nm	Φ_{PL}[b]	τ/ns[c]	$<r>$
1	338 (3.9×10^4)	395	0.804	0.83	0.12
2	332 (5.2×10^4)	386	0.030	—	0.07
3	353 (4.1×10^4)	391 and 410	0.839	0.77	0.13
4	338 (7.4×10^4)	385	0.015	—	0.07
5	331 (8.2×10^4)	403	0.706	0.95	0.06
6	331 (11×10^4)	385	0.016	—	0.11

[a]Units=$mol^{-1}\,cm^{-1}$. [b]Determined using quinine sulphate as standard. [c]Time of decay recorded only for **1**, **3** and **5**.

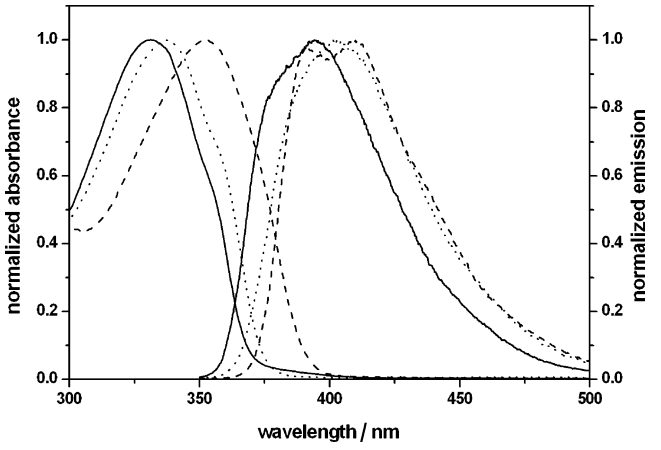


Figure 4. Absorption and photoluminescence spectra of compounds **1** (solid line), **3** (dashed line) and **5** (dotted line).

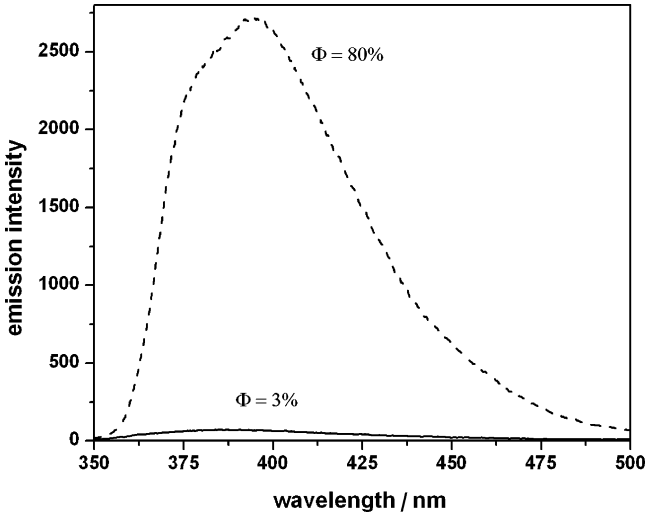


Figure 5. Photoluminescence spectra of compound **1** (dashed line) and **2** (solid line), showing the corresponding quantum yields. Experimental conditions: chloroform solution, λ_{exc}=340 nm, absorbance=0.06.

investigate solid state and LC phase luminescence, fabrication, and evaluation of OLEDs utilizing compounds **1**–**4** are currently under way.

4. Experimental section

4.1. *General*

^{1}H and ^{13}C NMR spectra were obtained with a Bruker AC-200F spectrometer at 200 MHz and 50.4 MHz, respectively, using TMS as the internal standard. IR spectra were recorded in KBr discs with a Perkin-Elmer model 283 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400CHN. Melting points, thermal transitions and mesomorphic textures were determined using an Olympus BX50 microscope in conjunction with a Mettler Toledo FP-90 heating stage and an exposure control unit PM-30. DSC measurements were carried out using Shimadzu equipment with a DSC-50 module. A Hitachi UV-Vis model 3000 spectrophotometer was used to measure absorption spectra. Fluorescence spectra were recorded on a Hitachi-F4500. Fluorescence decays 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.

4.2. *Materials*

All reagents and other chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The intermediates 1-decyloxy-4-ethynylbenzene (**15**), 1-decyloxy-4-ethynyl-2-nitrobenzene (**16**), 1-decyloxy-4-iodobenzene and 4-decyloxybenzonitrile were prepared according to a published procedure [47]. Organic solvents were of commercial grade quality except THF (HPLC grade); all were dried by traditional methods. Analytical thin layer chromatography (TLC) was conducted on Merck aluminium plates with 0.2 mm thickness of silica gel 60F-254.

4.3. *Synthesis*

4.3.1. 5-(4-Decyloxyphenyl)tetrazole 7. 4-Decyloxybenzonitrile (24 g, 92.57 mmol), 18.04 g (277.5 mmol) of sodium azide and 14.84 g (277.5 mmol) of ammonium chloride in 100 ml of dimethylformamide (DMF) were stirred overnight at 100°C. After cooling, the reaction mixture was poured into ice-water (400 ml) and acidified with 6N HCl (*caution: hydrazoic acid is formed!*). The precipitate was isolated by filtration, washed several times with water and dried to give 23.1 g (83%) of **7**, m.p. (EtOH/H_2O) 154.9–155.0°C. Calcd. for $C_{17}H_{26}N_4O$, C 67.52, H 8.67, N 18.53; found, C 67.91, H 8.66, N 19.09%.

4.3.2. 5-(4-Bromophenyl)tetrazole 8. The procedure of §4.3.1 was followed using 10 g (55 mmol) of 4-bromobenzonitrile, 10.72 g (165 mmol) of sodium azide and 8.82 g (165 mmol) of ammonium chloride; yield 12.1 g (98%), m.p. (EtOH/H_2O) 260.6–261.0°C. Calcd. for $C_7H_5BrN_4$, C 37.36, H 2.24, N 24.9; found, C 37.25, H 2.23, N 24.43%.

4.3.3. 2-(4-Bromophenyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole 9. 4-Bromobenzoic acid (2.0 g, 9.9 mmol) in thionyl chloride (10 ml) was heated under reflux overnight. The excess of thionyl chloride was removed by vacuum distillation, and the reaction mixture cooled to room temperature. 30 ml of pyridine and 2.72 g (9.0 mmol) of 5-(4-decyloxyphenyl)tetrazole were then added to the reaction flask containing 4-bromobenzoyl chloride and the mixture heated under reflux for 18 h. After cooling, the solution was poured into water (200 ml) and the precipitate was filtered and further purified by crystallization from ethanol to give 2.8 g (68% yield) of product as a white powder. LC transitions: Cr 104.0 SmA 120.0 I(°C). IR (KBr) ν_{max}/cm^{-1}: 2919, 2850, 1607, 1473, 1249, 1011, 834, 734. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.03 (d, 2 H, J=9.01 Hz), 7.97 (d, 2 H, J=8.79 Hz), 7.65 (d, 2 H, J=8.24 Hz), 7.00 (d, 2 H, J=8.5 Hz), 4.02 (t, 2 H), 1.8 (m, 2 H), 1.27 (broad, 14 H), 0.88 (t, 3 H). Calcd. for $C_{24}H_{29}BrN_2O_2$, C 63.02, H 6.39, N 6.12; found, C 63.18, H 6.45, N 6.04%.

4.3.4. 2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole 10. To a round-bottomed flask containing 4-bromobenzoyl chloride (prepared as in §4.3.3), 30 ml of pyridine and 2.0 g (8.9 mmol) of compounds **8** were added and the mixture heated under reflux for 12 h. After cooling, the precipitate was filtered off and washed with water and ethanol to afford 3.1 g (91% yield) of product as white needles, m.p. 256.0–257.2°C. IR (KBr) ν_{max}/cm^{-1}: 1598, 1474, 1071, 1005, 833, 734. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.00 (d, 4H, J=8.5 Hz), 7.68 (d, 4H, J=8.5 Hz). Calcd for $C_{14}H_8Br_2N_2O$, C 44.25, H 2.12, N 7.37; found, C 44.02, H 2.11, N 7.23%.

4.3.5. 2-(4-Decyloxyphenyl)-5-[4-(4-decyloxyphenylethynyl)phenyl]-1,3,4-oxadiazole 1. To a three-necked round-bottomed flask with condenser and argon inlet–outlet, a mixture of 0.5 g (1.09 mmol) of compound **9**, $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol) and triphenylphosphine (TPP) (26.2 mg, 0.1 mmol) and triethylamine (TEA) (25 ml) was stirred under reflux for 45 min. 1-Decyloxy-4-ethynylbenzene (**15**) (0.309 g, 1.2 mmol) dissolved in 5 mL of TEA was then added dropwise. The reaction mixture was heated under reflux for a further 2.5 h, cooled to room temperature and filtered off through celite, washing with THF (80 ml). The solvents were evaporated and the residue recrystallized from ethanol to give a pink powder (0.338 g, 49%). IR (KBr) ν_{max}/cm^{-1}: 2920, 2848, 2209, 1606, 1503, 1464, 1247, 836. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08 (d, 2H, J=8.2 Hz), 8.05 (d, 2H, J=8.6 Hz), 7.63 (d, 2 H, J=8.3 Hz), 7.47 (d, 2 H, J=8.6 Hz), 7.01 (d, 2 H, J=8.7 Hz), 6.87 (d, 2 H, J=8.7 Hz), 4.0 (m, 4 H), 1.78 (m, 4 H), 1.27 (broad, 28 H), 0.88 (t, 6 H). ^{13}C NMR ($CDCl_3$, ppm): 162.67, 160.28, 133.87, 132.60, 129.33, 127.67, 127.31, 123.71, 116.72, 115.27, 93.28, 88.10, 68.95, 68.77, 32.57, 30.23, 29.83, 26.67, 23.35, 14.79. Calcd. For $C_{42}H_{54}N_2O_3$, C 79.46, H 8.57, N 4.41; found, C 79.24, H 8.36, N 4.30%.

4.3.6. 2-[4-(4-Decyloxy-3-nitrophenylethynyl)phenyl]-5-(4-decyloxyphenyl)-1,3,4-oxadiazole 2. The procedure of §4.3.5 was followed using 0.432 g (0.945 mmol) of compound **9** and 0.315 g (1.04 mmol) of 1-decyloxy-4-ethynyl-2-nitrobenzene (**16**). The solid was recrystallized from EtOH to afford a magenta powder (0.331 g, 52%). IR (KBr) ν_{max}/cm^{-1}: 2920, 2847, 1610, 1530, 1494, 1465, 1346, 1249, 1168, 834. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.12–8.01 (m, 5 H), 7.64 (broad, 3 H), 7.08–7.04 (m, 3 H), 4.13 (t, 2 H), 4.03 (t, 2 H), 1.81 (m, 4 H), 1.27 (broad, 28 H), 0.88 (t, 6 H). ^{13}C NMR ($CDCl_3$, ppm): 162.78, 153.26, 140.33, 137.64, 132.82, 129.43, 127.42, 126.55, 124.48, 116.64, 115.71, 115.52, 115.15, 90.34, 89.80, 70.63, 69.00, 32.60, 30.25, 30.04, 29.82, 29.54, 26.68, 26.49, 23.38, 14.82. Calcd for $C_{42}H_{53}N_3O_5$, C 74.20, H 7.86, N 6.18; found, C 74.69, H 8.16, N 5.91%.

4.3.7. 2,5-Bis-(4-ethynylphenyl)-1,3,4-oxadiazole 17. (a) *Palladium cross-coupling*. A stirred mixture (under argon) of compound **10** (3 g, 7.9 mmol), $PdCl_2(PPh_3)_2$ (55.3 mg, 0.079 mmol), CuI (7.43 mg, 0.039 mmol) and TPP (20.69 mg, 0.079 mmol) in 50 ml of TEA was heated at reflux for 1 h. 2-Methyl-3-butyn-2-ol (2.6 ml,

23.7 mmol) was added dropwise by funnel and the mixture heated under reflux for a further 3.5 h. The reaction mixture was then cooled to room temperature and filtered through celite, washing with THF (150 ml). The solvents were evaporated to give a light yellow solid of 2,5-bis[4-(3-hydroxy-3-methylbutyn-1-yl)phenyl]-1,3,4-oxadiazole. IR (KBr) ν_{max}/cm^{-1}: 3292, 2979, 2930, 1929, 1608, 1488, 1272, 1156, 961, 845. This solid was used without further purification.

(b) *Deprotection*. The intermediate obtained thus for was dissolved in 50 ml of toluene and a few pellets of NaOH were added. The system was stirred under reflux for 6 h. The reaction mixture was then filtered through celite, washing with 150 ml of toluene. The solvent was evaporated under vacuum, affording a light brown solid, which was recrystallized from EtOH/H_2O (5/1). The yield was 1.33 g (63% in two steps) of a dark yellow powder, m.p. 196.1–198.0°C (dec.). IR (KBr) ν_{max}/cm^{-1}: 3285, 1484, 847. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.09 (d, 4 H, J=8.34 Hz), 7.64 (d, 4 H, J=8.37 Hz), 3.26 (s, 2 H). Calcd. for $C_{18}H_{10}N_2O$, C 79.99, H 3.73, N 10.36; found, C 79.26, H 3.90, N 10.49%.

4.3.8. 2,5-Bis[4-(4-decyloxyphenylethynyl)phenyl]-1,3,4-oxadiazole 3. A mixture of 1-decyloxy-4-iodobenzene (0.662 g, 1.84 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol) in THF (8 ml) and TEA (20 ml) was degassed by rapid bubbling of dry argon for 20 min. Compound **17** (0.250 g, 0.92 mmol) was then added and the mixture stirred at room temperature under bubbling Ar for 4 h. The precipitate was filtered and washed with THF (5 ml). The residue, an orange powder, was washed with much water and recrystallized from THF/EtOH to afford 0.236 g (35%) of a pale yellow powder. IR (KBr) ν_{max}/cm^{-1}: 2919, 2851, 2211, 1600, 1508, 1470, 1282, 1249, 1020, 841. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.10 (broad, 4 H), 7.68–7.47 (m, 8 H), 6.91 (broad, 4 H), 3.98 (broad, 4 H), 1.79–1.28 (m, 32 H), 0.88 (t, 6 H). ^{13}C NMR ($CDCl_3$, ppm): 164.98, 160.30, 133.88, 132.64, 129.07, 127.48, 123.35, 115.27, 93.59, 88.30, 68.76, 32.54, 30.21, 26.65, 23.34, 14.77. Calcd. for $C_{50}H_{58}N_2O_3$, C 81.71, H 7.95, N 3.81; found, C 81.72, H 7.89, N 4.06%.

4.3.9. 2,5-Bis[4-(4-decyloxy-3-nitrophenylethynyl)phenyl]-1,3,4-oxadiazole 4. A mixture of 4-bromo-1-decyloxy-2-nitrobenzene (1.365 g, 3.81 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (1.9 mg, 0.01 mmol) and TPP (5.2 mg, 0.02 mmol) in TEA (30 ml) was heated at reflux under Ar for 40 min. The compound **17** (0.513 g, 1.9 mmol) was then added to the reaction mixture and the reflux continued overnight. The cold reaction mixture was filtered through celite, with $CHCl_3$ (150 ml) washing. The solvents were evaporated and the residue recrystallized from isopropanol/$CHCl_3$ to give 0.824 g (53%) of an orange powder. IR (KBr) ν_{max}/cm^{-1}: 2921, 2850, 1611, 1531, 1498, 1465, 1343, 1263, 1162, 835. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.02–8.15 (m, 6 H), 7.65–7.68 (m, 6 H), 7.04–7.08 (broad, 2 H), 4.13 (t, 4 H), 1.85 (m, 4 H), 1.27 (broad, 28 H), 0.88 (t, 6 H). ^{13}C NMR ($CDCl_3$, ppm): 164.88, 153.29, 140.29, 137.64, 133.15, 132.85, 129.45, 129.01, 127.57, 126.96, 124.01, 115.38, 115.12, 90.59, 89.67, 70.61, 32.58, 30.29, 30.02, 29.93, 29.52, 26.46, 23.36, 14.81. Calcd. for $C_{50}H_{56}N_4O_7$, C 72.79, H 6.84, N 6.79; found, C 72.63, H 7.01, N 6.56%.

4.3.10. 1,3-Bis[5-(4-bromophenyl)-1,3,4-oxadiazole-2-yl] benzene 18. Isophthalic acid (2.0 g, 12.04 mmol) in 10 ml of thionyl chloride was heated at reflux overnight. Excess thionyl chloride was removed by vacuum distillation, and to the remaining residue 30 ml of pyridine and 5.95 g (26.49 mmol) of 5-(4-bromophenyl)tetrazole were added. The mixture was heated at reflux for 2 days. After cooling, the precipitate was filtered off and washed with water and hot ethanol to give 5.8 g (92% yield) of a white powder, m.p. 293.4–294.0°C. IR (KBr) ν_{max}/cm^{-1}: 1597, 1545, 1473, 1250, 1072, 1004, 836, 729. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.88 (s, 1 H), 8.36 (dd, 2 H, J=7.8 and 1.6 Hz), 8.07 (d, 4 H, J=8.5 Hz), 7.73 (m, 5 H). Calcd. for $C_{22}H_{12}Br_2N_4O_2$, C 50.41, H 2.31, N 10.69; found, C 50.40, H 2.17, N 10.40%.

4.3.11. 1,3-Bis[5-(4-ethynylphenyl)-1,3,4-oxadiazole-2-yl]benzene 19. (a) *Palladium cross-coupling*. A mixture of compound **7** (3.0 g, 5.73 mmol), $PdCl_2(PPh_3)_2$ (42.5 mg, 0.06 mmol), CuI (5.7 mg, 0.03 mmol) and TPP (15.7 mg, 0.06 mmol) in 40 ml of DMA/TEA 5/2 under argon, was held at 115°C for 1 h. 2-Methyl-3-butyn-2-ol (1.6 ml, 14.32 mmol) was added dropwise to the reaction flask and the mixture was held at 115°C for a further 12 h. It was then cooled to room temperature and the precipitate filtered off and washed with water to give a dark yellow powder of 1,3-bis{5-[4-(3-hydroxy-3-methylbutyn-1-yl)phenyl]-1,3,4-oxadiazole-2-yl}benzene. IR (KBr) ν_{max}/cm^{-1}: 3290, 2977, 2928, 1608, 1552, 1489, 1265, 1159, 843. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.88 (s, 1 H), 8.35 (d, 2 H, J=7.8 Hz), 8.14 (d, 4 H, J=8.3 Hz), 7.75 (t, 1 H), 7.60 (d, 4 H, J=8.3 Hz), 2.08 (s, 2 H, OH), 1.66 (s, 12 H, CH_3).

(b) *Deprotection*. The intermediate obtained thus far and a few pellets of NaOH were stirred under reflux in 50 ml of toluene for 5 h. The reaction mixture was cooled and filtered through celite, washing with toluene (150 ml). The red solution was evaporated under vacuum affording a brown solid, which was recrystallized from MeOH/THF (80 ml) to give 1.33 g (56%) of

the product as a yellow powder. IR (KBr) ν_{max}/cm^{-1}: 3286, 1606, 1541, 1483, 1252, 1076, 842, 707. ^1H NMR ($CDCl_3$) δ (ppm): 8.87 (s, 1 H), 8.35 (d, 2 H, J=7.8 Hz), 8.15 (d, 4 H, J=8.2 Hz), 7.66–7.78 (m, 5 H), 3.27 (s, 2 H). ^{13}C NMR ($CDCl_3$): 165.2, 164.4, 133.5, 130.8, 130.6, 127.6, 126.6, 125.7, 125.6, 124.2, 83.3, 81.

4.3.12. 1,3-Bis{5-[4-(4-decyloxyphenyletynyl)phenyl]-1, 3,4-oxadiazole-2-yl]benzene 5. The procedure of § 4.3.8 was followed using 0.755 g (2.1 mmol) of 1-decyloxy-4-iodobenzene and 0.414 g (1.0 mmol) of compound **19**. Recrystallization from $CHCl_3$ (200 ml) and acetonitrile (150 ml) afforded 183 mg (21%) of a sand colour powder. IR (KBr) ν_{max}/cm^{-1}: 2920, 2849, 2210, 1599, 1507, 1463, 1244, 835. ^1H NMR ($CDCl_3$) δ (ppm): 8.9–6.87 (m, 20 H), 3.98 (t, 4 H), 1.8–1.27 (broad 28 H), 0.88 (t, 6 H). Calcd. for $C_{58}H_{62}N_4O_4$, C 79.24, H 7.11, N 6.37; found, C 79.50, H 7.18, N 6.67%.

4.3.13. 1,3-Bis{5-[4-(4-decyloxy-3-nitrophenyletynyl)-phenyl]-1,3,4-oxadiazole-2-yl]benzene 6. The procedure of § 5.3.9 was followed using 0.751 g (2.1 mmol) of 4-bromo-1-decyloxy-2-nitrobenzene and 0.414 g (1 mmol) of compound **19**. Time of reflux: 20 h. The mixture was filtered through celite, washing with $CHCl_3$ (150 ml). The solvents were evaporated and the residue recrystallized from acetonitrile/THF to give 0.147 g (15.2%) of a yellow powder. IR (KBr) ν_{max}/cm^{-1}: 2920, 2850, 2208, 1606, 1530, 1494, 1460, 1345, 1278, 1160, 1073, 1002, 833. ^1H NMR ($CDCl_3$) δ (ppm): 8.86 (s, 1 H), 8.34 (d, 2 H, J=7.8 Hz), 8.16 (d, 4 H, J=8.3 Hz), 8.01 (s, 2 H), 7.78–7.64 (m, 7 H), 7.06 (d, 2 H, J=8.8 Hz), 4.13 (t, 4 H), 1.85 (m, 4 H), 1.25 (broad, 28 H), 0.87 (t, 6 H). Calcd. for $C_{58}H_{60}N_6O_8$, C 71.88, H 6.24, N 8.67; found, C 71.30, H 6.80, N 8.31%.

Acknowledgements

The authors thank Mrs. Marly da Silveira Soldi (DSC measurements), Prof. Ted Ray Taylor and Prof. Frank Quina for helpful discussions. This work was supported by the agencies CNPq-Brazil and Funcitec/SC.

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