Sonogashira Coupling Applied in the Synthesis of 1,2,4-Oxadiazole-Based Nonsymmetrical Liquid Crystals

Hugo Gallardo,*[a] Rodrigo Cristiano,[a] André A. Vieira,[a] Ricardo A.W. Neves Filho,[b] Rajendra M. Srivastava*[b]

[a] Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil
Fax +55(48)37216850 ; E-mail: hugo@qmc.ufsc.br

[b] Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, PE 50740-540, Brazil

Received 9 October 2007; revised 22 November 2007

Abstract: A series of highly π-conjugated nonsymmetrical liquid crystals, based on the core 3,5-(disubstituted)-1,2,4-oxadiazole with a shape similar to a hockey stick, were successfully synthesized by convergent Sonogashira coupling reaction between the building blocks of aryl iodides and the corresponding terminal arylacetylenes, using 3-[4-(decyloxy)phenyl]-5-(haloaryl)-1,2,4-oxadiazoles or decyl 4-iodobenzoate (**10**) and terminal arylacetylenes. This versatile synthetic route yielded luminescent mesogens with smectic and nematic phases, typical of calamitic compounds.

Key words: Sonogashira coupling, liquid crystals, 1,2,4-oxadiazoles, acetylenes

In an attempt to optimize molecular properties for display and optical applications, considerable attention has been given to the design and synthesis of liquid crystalline compounds with suitable selection of the core fragment, linking group, and terminal functionality.[1] Highly π-conjugated liquid crystal molecules containing heterocycles have attracted increasing interest in the field of organic light emitting diodes (OLEDs), where electron-deficient heteroaromatic rings can lead to a good charge-transporting materials allied with its inherent self-organization ability, and strong fluorescence.[2] 1,3,4-Oxadiazole-based liquid crystals with high thermal stability and very efficient blue luminescence have been synthesized.[3] In addition, the carbon–carbon triple bond is a good spacer group in liquid crystals, which produces a highly π-polarizable and conjugated moiety. Liquid crystals containing a carbon–carbon triple bond are very interesting materials due to their large birefringence,[4] large index of refraction parallel to the director, large electric polarizability and the ability to form optical films transparent in the visible. The Sonogashira coupling[5] between aryl halides and terminal acetylenes, the most common employed synthetic technique to build carbon–carbon triple bonds, has been widely used in the synthesis of functional materials.[6]

Herein, we report an efficient synthesis of a series of liquid crystalline compounds **1a–f**, which possess a 1,2,4-oxadiazole heterocyclic nonsymmetrical core and similar hockey stick shape (Figure 1).[7] In our attempts to gain a better understanding of the chemical structure versus thermal/optical property relationships, different aromatic moieties were linked to the central core by a carbon–carbon triple bond. These aromatic groups [phenyl, 2-naphthyl, 4-(piperazin-1-yl)phenyl, or 4-(alkoxycarbonyl)phenyl], were chosen by considering an elongation of the liquid crystal molecule rod, thus increasing the length-to-breadth ratio, and also an extension in the π-conjugated system, with strong electron-donating (e.g., OR, NR_2) and electron-withdrawing (e.g., NO_2, C=O) substituents.

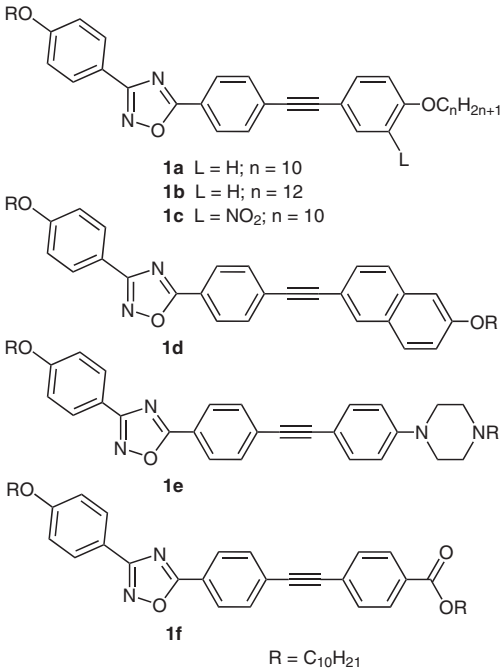


Figure 1 Structures of the final synthesized compounds **1a–f**

The initial synthesis of the intermediates containing the 1,2,4-oxadiazole ring (compounds **6a**,**b**) was carried out as shown in Scheme 1. First, *N*-hydroxyimidamide **3** was prepared from 4-(decyloxy)benzonitrile (**2**)[8] by the Tiemann reaction[9] using hydroxylamine hydrochloride, and potassium hydroxide in a methanol–water mixture.

The formation of the 1,2,4-oxadiazole ring was accomplished by the reaction between *N*-hydroxyimidamide **3** and the freshly prepared acyl chlorides **5a**,**b** in pyridine under reflux, affording the bromide and iodide derivatives **6a**,**b** in 95% and 65% yields, respectively.

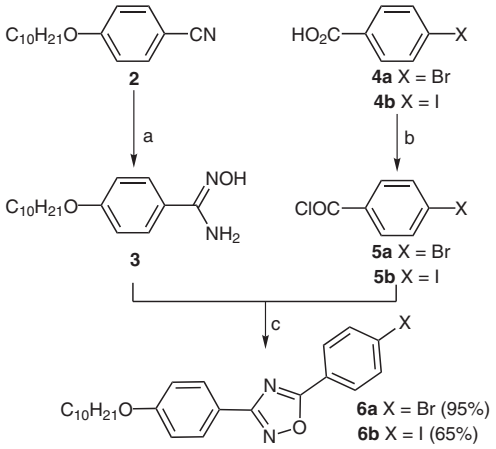
The synthesis of the final compounds **1a–e** is outlined in Scheme 2. The terminal arylacetylenes **7a–e** were ob-

SYNTHESIS 2008, No. 4, pp 0605–0609
Advanced online publication: 31.01.2008
DOI: 10.1055/s-2008-1032156; Art ID: M07407SS

Table 1 Sonogashira Coupling Results, Optical Data, and Liquid Crystalline Profile of Final Compounds **1a–e**

Compd	Yield (%)	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	Transition temperatures[b] (°C)
1a	81	333	413	Cr 104 SmC 169 N 195 I
1b	82	333	412	Cr 105 SmC 162 N 184 I
1c	74	321	390	Cr 86 SmC 149 SmA 158 I
1d	80	346	437	Cr 102 SmC 190 N 228 I
1e	77	349	468	Cr 124 SmC 171 SmA 256 I[c]
1f	81	320	413	Cr 99 SmC 162 N 177 I

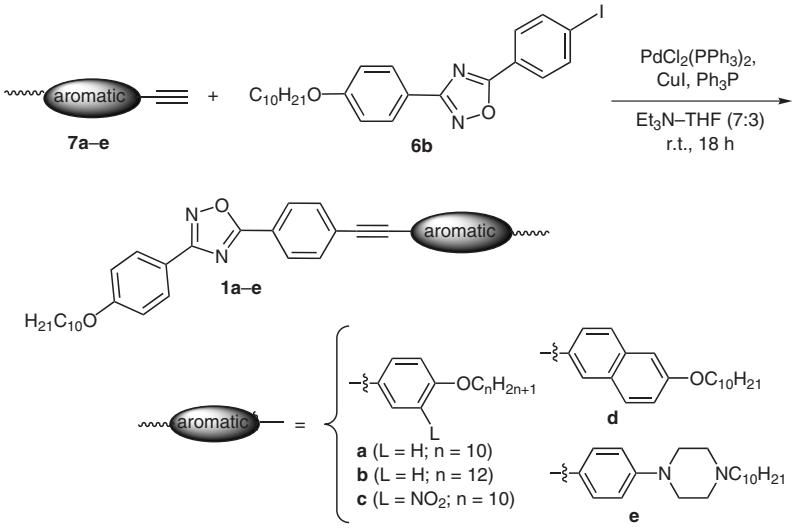
[a] In $CHCl_3$ soln.
[b] Observed by optical microscopy on heating. Cr = crystal phase; SmC = smectic C phase; SmA = smectic A phase; N = nematic phase; I = isotropic liquid.
[c] Decomposition starts.



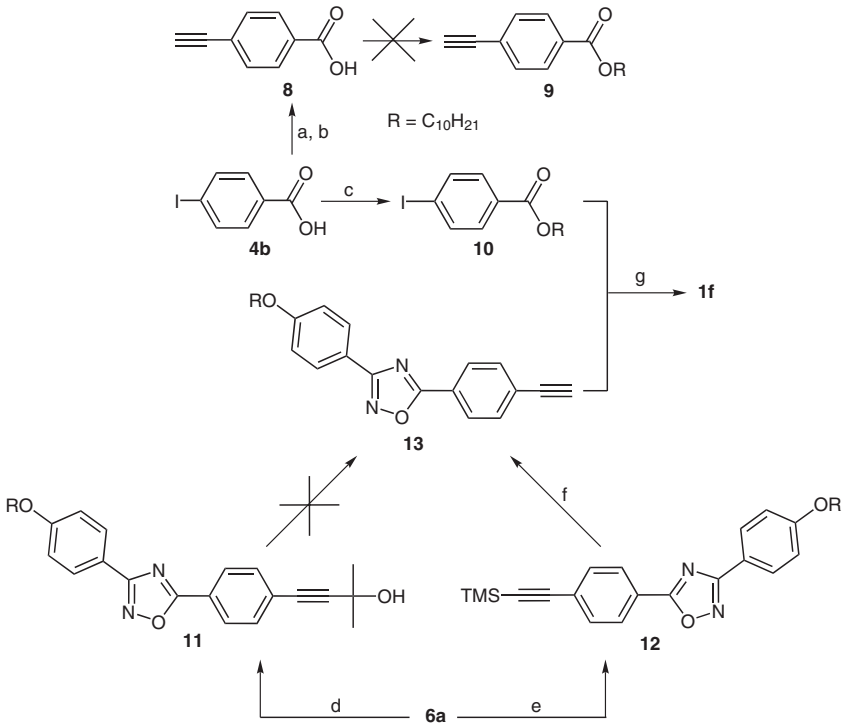
Scheme 1 *Reaction conditions*: (a) $NH_2OH{\cdot}HCl$, MeOH–H_2O (1:1), reflux, 12 h, 85%; (b) $SOCl_2$, CH_2Cl_2, reflux, 18 h, 100%; (c) pyridine, reflux 16 h.

tained from their respective aryl halides via Sonogashira coupling with commercially available 2-methylbut-3-yn-2-ol followed by protective group elimination. Compounds **1a–e** were synthesized by Sonogashira coupling between an aryl iodide containing the 1,2,4-oxadiazole ring (compound **6b**) and the respective terminal arylacetylenes **7a–e**. These reactions were carried out using 10 mol% of the catalyst dichlorobis(triphenylphosphine)palladium, 5 mol% of the co-catalyst copper (I) iodide, and triphenylphosphine as an additive, in a triethylamine–tetrahydrofuran mixture (7:3). All reactions were carried out at room temperature due to the better reactivity of the aryl iodide compared to the aryl bromide for Sonogashira coupling. The reaction yields for the Sonogashira coupling are shown in Table 1.

As demonstrated in Scheme 3, attempts to esterify carboxylic acid **8** to obtain the terminal arylacetylene **9** failed. This may be due to the high instability of compound **8**, which easily polymerizes on heating.[10] Thus, a different approach was necessary for the synthesis of the final compound **1f**. In this case we simply reversed the functionalities, building the carbon–carbon triple bond on the part of the molecule containing the heterocycle. Firstly, this was attempted by the reaction of **6a** with 2-methylbut-3-yn-2-ol, which gave the respective alkynol **11**. However, in the deprotection step using the protocol of Trofimov et al.[11] the arylacetylene product was not formed, and decomposition in the reaction media was also observed. The synthesis was then performed by Sonogashira coupling of aryl bromide **6a** with (trimethylsilyl)acetylene giving intermediate **12** in 80% yield. The elimination of the trimethylsilyl group was carried out by reaction with potassium carbonate in a mixture of methanol and dichloromethane at room temperature, affording the terminal arylacetylene **13** in 98% yield. The final step consisted of the Sonogashira coupling, under the same conditions as those used for the other final compounds **1a–e**, between arylacetylene **13** and decyl 4-iodobenzoate (**10**), obtained from the Fischer esterification of acid **4b**, to give compound **1f**.



Scheme 2



Scheme 3 *Reaction conditions*: (a) EtOH, H_2SO_4 (cat.), toluene, reflux, 7 h, 87%; (b) (i) 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, Ph_3P, Et_3N–THF (2:3), reflux, 3 h; (ii) KOH, *i*-PrOH, reflux 7 h, 59%; (c) decan-1-ol, H_2SO_4 (cat.), toluene, reflux, 18 h, 82%; (d) 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, Ph_3P, Et_3N–pyridine, reflux, 3 h; (e) (trimethylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, Ph_3P, Et_3N–pyridine, 50 °C, 24 h, 80%; (f) K_2CO_3, CH_2Cl_2–MeOH, r.t., 98%; (g) $PdCl_2(PPh_3)_2$, CuI, Ph_3P, Et_3N–THF (3:1), r.t., 20 h, 81%.

The structures of all synthesized compounds were fully characterized by IR, ^1H and ^{13}C NMR spectra, and elemental analysis.

A preliminary study of the liquid crystalline profile of the final molecules **1a–f** was performed by polarizing optical microscopy (POM), and the results are shown in Table 1. All these compounds exhibited liquid crystal phases, in particular the smectic C (SmC) and nematic (N) phases with Schilieren textures, typical of calamitic compounds. In contrast, compounds **1c** and **1e** did not show nematic phase, and the smectic A phase observed presented a fan-shaped texture. This may be explained by the presence of a lateral nitro group and piperazine ring, respectively, which increased the lateral interaction and lead to a layered phase.

With exception of compound **1c**, which showed very poor fluorescence due to the nitro lateral group, all the other final compounds exhibited strong blue fluorescence with maximum emission wavelengths between 410 and 470 nm. The absorption and emission spectra data in chloroform solution are listed in Table 1.

In summary, we successfully employed a palladium-catalyzed cross-coupling reaction (Sonogashira reaction) to prepare nonsymmetrical liquid crystalline compounds based on 5-[4-(arylethynyl)phenyl]-3-[4-(decyloxy)phenyl]-1,2,4-oxadiazole; they possess a similar hockey-stick-shaped structure. These final compounds **1a–f** showed liquid crystal phases, in particular smectic and nematic phases typical of calamitic structures, observed by polarizing optical microscopy analysis. They also exhibited strong blue fluorescence in solution.

All reagents were obtained from commercial sources and used without further purification. Chromatography was performed using silica gel (60–120 mesh). IR spectra were recorded on a Perkin-Elmer model 283 spectrophotometer in KBr discs. ^1H NMR spectra were obtained with a Varian Mercury Plus 400-MHz instrument using TMS as the internal standard. ^{13}C NMR spectra were recorded on a Varian Mercury Plus 100 MHz spectrometer. Elemental analysis was performed with a Carlo Erba instrument model E-1110. The melting points, thermal transitions, and mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot-stage and a PM-30 exposure control unit. An HP UV-vis model 8453 spectrophotometer was used to record absorption spectra. Fluorescence spectra were recorded on a Hitachi-F-4500. Sonogashira couplings were carried out under an argon atmosphere. Terminal arylacetylenes **7a–e** were prepared according to published methods.[3c,12]

4-(Decyloxy)-*N*-hydroxybenzimidamide (3)

This intermediate was synthesized following the published procedure for 4-alkoxy-*N*-hydroxybenzimidamide;[13] yield: 85%; mp 109–110 °C.

IR (KBr): 3447, 3348, 2919, 2852, 1651, 1609, 1391, 1252, 826. cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.34 (s, 1 H), 5.15 (s, 2 H), 3.93 (t, *J* = 6.8 Hz, 2 H), 1.81 (q, *J* = 6.8 Hz, 2 H), 1.77 (m, 2 H), 1.27 (m, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

Anal. Calcd for $C_{17}H_{28}N_2O_2$: C, 69.83; H, 9.65; N, 9.58. Found: C, 69.26; H, 9.91; N, 9.33.

3-[4-(Decyloxy)phenyl]-5-(4-iodophenyl)-1,2,4-oxadiazole (6b); Typical Procedure

Freshly prepared 4-iodobenzoyl chloride[14] (**5b**, 1.41 g, 5.3 mmol) and **3** (1.6 g, 5.5 mmol) were stirred under reflux in pyridine for 16 h. After cooling, the mixture was poured into cold H_2O. The precipitate was then filtered and recrystallized (EtOH) to give light brown crystals; yield: 65%; mp 104 °C.

IR (KBr): 2923, 2853, 1606, 1477, 1262, 1360 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 9.2 Hz, 2 H), 7.92 (s, 4 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 1.81 (m, 2 H), 1.43 (m, 2 H), 1.28 (m, 12 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 169.0, 161.9, 138.6, 129.6, 129.3, 124.0, 119.1, 115.0, 100.2, 68.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3.

Anal. Calcd for $C_{24}H_{29}IN_2O_2$: C, 57.15; H, 5.80; N, 5.55. Found: C, 57.01; H, 5.20; N, 5.13.

5-(4-Bromophenyl)-3-(4-(decyloxy)phenyl)-1,2,4-oxadiazole (6a)

Following the typical procedure for **6b** using 4-bromobenzoyl chloride (**5a**) gave **6a** as colorless crystals; yield: 2.08 g (95%); Cr 90 °C N, 109 °C I.

IR (KBr): 2916, 2851, 1598, 1477, 1359, 1253, 1014, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 4 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 4.02 (t, 2 H), 1.81 (m, 2 H), 1.27 (m, 14 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.5, 168.8, 161.7, 129.4, 128.5, 128.1, 127.5, 123.4, 118.9, 114.7, 68.2, 21.9, 29.5, 29.4, 29.2, 26.0, 22.7, 14.1.

Anal. Calcd for $C_{24}H_{29}BrN_2O_2$: C, 63.02; H, 6.39; N, 6.12. Found: C, 62.98; H, 6.21; N, 6.25.

Synthesis of 1a–e; General Procedure

A mixture of **6b** (0.3 g, 0.6 mmol), $PdCl_2(PPh_3)_2$ (41.66 mg, 0.06 mmol). and Ph_3P (15.59 mg, 0.06 mmol) in Et_3N–THF (7:3, 30 mL) was stirred at r.t. for 15 min. CuI (5.65 mg, 0.03 mmol) was then added and the mixture was further stirred for 20 min. The corresponding terminal arylacetylene **7a–e** (0.71 mmol) dissolved in Et_3N (5 mL) was added dropwise and the mixture was stirred at r.t. for 16 h. The progress of the reaction was followed by TLC (hexane–EtOAc, 95:5). The mixture was filtered through a Celite pad and washed with THF (50 mL). The solvents were evaporated under reduced pressure and the crude product was recrystallized (hexanes–$CHCl_3$) to afford the desired product.

3-[4-(Decyloxy)phenyl]-5-(4-{[4-(decyloxy)phenyl]ethynyl}phenyl)-1,2,4-oxadiazole (1a)

Yield: 81%.

IR (KBr): 2919, 2849, 2204, 1597, 1505, 1248, 840 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.4 Hz, 2 H), 8.10 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 4.02 (m, 4 H), 1.81 (m, 4 H), 1.28 (m, 28 H), 0.89 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 169.0, 161.8, 159.9, 133.5, 132.1, 129.3, 128.2, 123.5, 119.3, 114.9, 114.8, 93.4, 87.6, 86.8, 68.3, 32.1, 29.8, 29.5, 29.4, 26.2, 22.9, 14.4.

Anal. Calcd for $C_{42}H_{54}N_2O_3$: C, 79.46; H, 8.57; N, 4.41. Found: C, 79.62; H, 8.42; N, 4.07.

3-[4-(Decyloxy)phenyl]-5-(4-{[4-(dodecyloxy)phenyl]ethynyl}phenyl)-1,2,4-oxadiazole (1b)

Yield: 82%.

IR (KBr): 2920, 2851, 2206, 1597, 1597, 1250, 840 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.0 Hz, 2 H), 8.10 (d, *J* = 8.2 Hz, 2 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 4.01 (m, 4 H), 1.81 (m, 4 H), 1.27 (m, 32 H), 0.86 (t, *J* = 5.6 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 162.4, 159.9, 133.5, 132.1, 130.9, 129.3, 129.1, 128.2, 123.5, 119.3, 115.0, 114.8, 93.4, 87.6, 68.4, 46.3, 32.1, 29.9, 29.6, 29.4, 26.2, 22.9, 14.3.

Anal. Calcd for $C_{44}H_{58}N_2O_3$: C, 79.72; H, 8.82; N, 4.23. Found: C, 79.22; H, 8.61; N, 4.15.

5-(4-{[4-(Decyloxy)-3-nitrophenyl]ethynyl}phenyl)-3-[4-(decyloxy)phenyl]-1,2,4-oxadiazole (1c)

Yield: 74%.

IR (KBr): 2922, 2849, 2207, 1607, 1535, 1356, 1261, 1016, 846 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.0 Hz, 2 H), 8.09 (d, *J* = 8.0 Hz, 2 H), 7.91 (s, 1 H), 7.67 (m, 3 H), 7.07 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 4.13 (t, *J* = 6.4 Hz, 2 H), 4.02 (t, *J* = 6.6 Hz, 2 H), 1.82 (m, 4 H), 1.28 (m, 28 H), 0.88 (t, *J* = 6.4 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 169.0, 161.8, 152.9, 138.6, 137.2, 132.3, 129.6, 129.3, 129.0, 128.3, 127.3, 124.2, 119.2, 115.0, 114.9, 114.7, 90.4, 89.2, 70.2, 68.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.48, 29.4, 29.1, 26.0, 22.9, 14.4.

Anal. Calcd for $C_{42}H_{53}N_3O_5$: C, 74.20; H, 7.86; N, 6.18. Found: C, 74.11; H, 7.56; N, 6.07.

5-(4-{[6-(Decyloxy)naphthalen-2-yl]ethynyl}phenyl)-3-[4-(decyloxy)phenyl]-1,2,4-oxadiazole (1d)

Yield: 80%.

IR (KBr): 2919, 2847, 1606, 1465, 1364, 1253, 1172, 1021, 842 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 2 H), 8.11 (d, *J* = 8.8 Hz, 2 H), 8.02 (s, 1 H), 7.74–7.70 (m, 4 H), 7.55 (dd, *J* = 8.8, 1.1 Hz, 1 H), 7.19 (dd, *J* = 8.8, 2.1 Hz, 1 H), 7.12 (d, *J* = 2.1 Hz, 1 H), 7.01 (d, *J* = 8.8, 2 H), 4.08 (t, *J* = 6.0 Hz, 2 H), 4.03 (t, *J* = 6.6 Hz, 2 H), 1.84 (m, 4 H), 1.48 and 1.27 (m, 28 H), 0.89 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 169.0, 161.8, 158.4, 134.7, 132.3, 131.9, 129.6, 129.3, 129.0, 128.3, 127.1, 123.7, 120.1, 119.3, 117.4, 114.9, 106.8, 93.9, 88.5, 68.4, 32.1, 29.8, 28.8, 29.6, 29.5, 29.4, 26.3, 26.26, 22.9, 17.8, 14.4.

Anal. Calcd for $C_{46}H_{56}N_2O_3$: C, 80.66; H, 8.24; N, 4.09. Found: C, 80.72; H, 8.80; N, 4.23.

3-[4-(Decyloxy)phenyl]-5-(4-{[4-(4-decylpiperazin-1-yl)phenyl]ethynyl}phenyl)-1,2,4-oxadiazole (1e)

Yield: 77%.

IR (KBr): 2921, 2848, 2208, 1602, 1514, 1357, 1246, 816, 759 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.0 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 3.49 (t, *J* = 6.4 Hz, 4 H), 3.15 (q, *J* = 7.2 Hz, 2 H), 2.91 (t, *J* = 6.4 Hz, 4 H), 2.66 (m, 2 H), 1.81 (m, 2 H), 1.26 (m, 28 H), 0.88 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 168.9, 161.8, 150.6, 133.2, 132.1, 129.3, 128.2, 123.3, 119.2, 115.7, 114.9, 113.5, 93.7, 87.8, 68.4, 58.6, 47.3, 46.3, 32.1, 29.9, 29.6, 29.5, 29.5, 29.4, 27.4, 26.2, 25.6, 22.9, 14.36, 8.8.

Anal. Calcd for $C_{46}H_{62}N_4O_2$: C, 78.59; H, 8.89; N, 7.97. Found: C, 78.81; H, 8.57; N, 7.56.

3-[4-(Decyloxy)phenyl]-5-{4-[(trimethylsilyl)ethynyl]phenyl}-1,2,4-oxadiazole (12)

A mixture of **6a** (2 g, 4.4 mmol), $PdCl_2(PPh_3)_2$ (30.00 mg, 0.04 mmol), Ph_3P (10.48 mg, 0.04 mmol), CuI (5.65 mg, 0.03 mmol), and (trimethylsilyl)acetylene (0.59 g, 6.0 mmol) in Et_3N–pyridine (8:2, 50 mL) was stirred at 50 °C for 24 h. The progress of the reaction was followed by TLC (hexane–EtOAc, 95:5). The mixture was filtered through a Celite pad and washed with THF (100 mL). The solvents were vaporized under reduced pressure and the crude product was recrystallized (EtOH); yield: 80%; mp 107–108 °C.

IR (KBr): 2920, 2850, 2154, 1610, 1466, 1263, 844, 760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.0 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 4.03 (t, *J* = 6.4 Hz, 2 H), 1.82 (m, 2 H), 1.28 (m, 14 H), 0.89 (t, *J* = 6.4 Hz, 3 H), 0.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 168.9, 161.7, 132.6, 129.2, 132.6, 129.2, 128.0, 127.7, 124.0, 119.1, 114.9, 104.0, 98.4, 68.3, 32.1, 29.7, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3, 0.0.

Anal. Calcd for $C_{29}H_{38}N_2O_2Si$: C, 73.37; H, 8.07; N, 5.90. Found: C, 73.64; H, 8.33; N, 6.10.

3-[4-(Decyloxy)phenyl]-5-(4-ethynylphenyl)-1,2,4-oxadiazole (13)

Compound **12** (1 g, 2.1 mmol) and K_2CO_3 (0.58 g, 4.2 mmol) in CH_2Cl_2–MeOH (3:2) were vigorously stirred overnight at r.t. The mixture was filtered and solvents evaporated under reduced pressure to give the crude product, which was purified by recrystallization (EtOH); yield: 98%; Cr 93 °C N, 107 °C I.

IR (KBr): 3279, 2923, 2851, 1612, 1266, 846, 760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.0 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 3.28 (s, 1 H), 1.81 (m, 2 H), 1.28 (m, 14 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 169.0, 161.8, 132.9, 129.3, 128.2, 126.7, 124.5, 119.1, 114.9, 82.8, 80.7, 77.6, 77.2, 76.9, 68.4, 32.1, 29.9, 29.6, 29.4, 26.2, 22.9, 14.3.

Anal. Calcd for $C_{26}H_{30}N_2O_2$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.19; H, 7.73; N, 6.67.

Decyl 4-Iodobenzoate (10)

In a round-bottom flask coupled with a Dean–Stark apparatus, a mixture of 4-iodobenzoic acid (**4b**, 1 g, 4.0 mmol), decan-1-ol (0.97 g, 6.1 mmol), and H_2SO_4 (catalytic amount) in toluene was refluxed for 18 h. The reaction was completed when 0.1 mL of H_2O was trapped. The solvents were concentrated under reduced pressure, then the crude product was purified by column chromatography (silica gel, hexane–EtOAc, 8:2) to afford **10** as a brown oil; yield: 1.28 g (82%).

IR (KBr): 2922, 2853, 1721, 1586, 1272, 1108, 753 cm^{-1}.

Decyl 4-[(4-{3-[4-(Decyloxy)phenyl]-1,2,4-oxadiazol-5-yl}phenyl)ethynyl]benzoate (1f)

A mixture of **10** (0.1 g, 0.25 mmol), $PdCl_2(PPh_3)_2$ (18 mg, 0.03 mmol), and Ph_3P (7.00 mg, 0.03 mmol) in Et_3N–THF (7:3, 30 mL) was stirred at r.t. for 15 min. CuI (5.65 mg, 0.03 mmol) was then added as solid and the mixture was stirred for an additional 20 min. Compound **13** (0,2 g, 0.5 mmol) dissolved in THF (8 mL) was added dropwise. The mixture was stirred at r.t. for 20 h. The progress of the reaction was followed by TLC (hexane–EtOAc, 95:5). The mixture was filtered through a Celite pad and washed with THF (50 mL). The filtrate was concentrated under reduced pressure to give the crude product, which was recrystallized (hexane–$CHCl_3$) to afford the product; yield: 81%.

IR (KBr): 2919, 2849, 1710, 1609, 1467, 1272, 1108, 841, 762 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 2 H), 8.09 (d, *J* = 8.8 Hz, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 4.33 (t, *J* = 6.4 Hz, 2 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 1.79 (m, 4 H), 1.28 (m, 28 H), 0.88 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.9, 169.0, 166.2, 161.8, 132.5, 131.8, 130.6, 129.8, 129.3, 127.3, 124.3, 119.1, 114.9, 92.0, 91.3, 92.1, 91.4, 68.4, 65.7, 46.1, 32.1, 29.8, 29.8, 29.6, 29.5, 28.9, 26.2, 22.9, 14.3, 8.9.

Anal. Calcd for $C_{43}H_{54}N_2O_4$: C, 77.91; H, 8.21; N, 4.23. Found: C, 77.65; H, 8.32; N, 4.37.

Acknowledgment

The authors thank to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) and Merck (Germany) for funding.

References

(1) (a) Spieker, B.; Hahn, A.; Vill, V. *Synthesis* **2002**, 2129. (b) Feuerbacher, N.; Vögtle, F.; Windscheidt, J.; Poetsch, E.; Nieger, M. *Synthesis* **1999**, 117. (c) Pickaert, G.; Ziessel, R. *Synthesis* **2004**, 2716. (d) Lee, A. S. Y.; Wu, C. C.; Lin, L. S.; Hsu, H. F. *Synthesis* **2004**, 568. (e) Lee, S. K.; Naito, Y.; Shi, L.; Tokita, M.; Takezoe, H.; Watanabe, J. *Liq. Cryst.* **2007**, 935. (f) Prajapati, A. K.; Patel, H. N. *Liq. Cryst.* **2007**, 903.

(2) (a) Vlachos, P.; Mansoor, B.; Aldred, M. P.; O'Neill, M.; Kelly, S. M. *Chem. Commun.* **2005**, 2921. (b) O'Neill, M.; Kelly, S. M. *Adv. Mater. (Weinheim, Ger.)* **2003**, 1135.

(3) (a) Cristiano, R.; Santos, D. M. P. O.; Gallardo, H. *Liq. Cryst.* **2005**, 7. (b) Cristiano, R.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2005**, 15. (c) Cristiano, R.; Vieira, A. A.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2006**, 381. (d) Gallardo, H.; Magnago, R.; Bortoluzzi, A. J. *Liq. Cryst.* **2001**, 1343.

(4) Wu, S.-T.; Finkenzeller, U.; Rieffenrath, J. J. *Appl. Phys.* **1989**, 4372.

(5) (a) Sonogashira, K. *J. Organomet. Chem.* **2002**, 46. (b) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874.

(6) (a) Vieira, A. A.; Cristiano, R.; Bortoluzzi, A. J.; Gallardo, H. *J. Mol. Struct.* **2007**, in press; DOI: 10.1016/j.molstruc.2007.05.006. (b) Vasconcelos, U. B.; Dalmolin, E.; Merlo, A. A. *Org. Lett.* **2005**, *7*, 1027. (c) Tong, L. H.; Pascu, S. I.; Jarrosson, T.; Sanders, J. K. M. *Chem. Commun.* **2006**, 1085.

(7) Dingemans, T. J.; Murthy, N. S.; Samulski, E. T. *J. Phys. Chem. B* **2001**, 8845.

(8) Lee, J. W.; Kang, S. U.; Lim, J. O.; Choi, H. K.; Jin, M. K.; Toth, A.; Pearce, L. V.; Tran, R.; Wang, Y.; Szabo, T.; Blumberg, P. M. *Bioorg. Med. Chem.* **2004**, *12*, 371.

(9) Tiemann, F. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 126.

(10) Melissaris, A. P.; Litt, M. H. *J. Org. Chem.* **1992**, *57*, 6998.

(11) Mal'kina, A. G.; Brandsma, L.; Vasilevsky, S. F.; Trofimov, B. A. *Synthesis* **1986**, 589.

(12) (a) Merlo, A. A.; Braun, J. E.; Vasconcelos, U. B.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2000**, 657. (b) Ely, F.; Conte, G.; Merlo, A. A.; Gallardo, H. *Liq. Cryst.* **2004**, 1413.

(13) Grassmann, S.; Sadek, B.; Ligneau, X.; Elz, S.; Ganellin, C. R.; Arrang, J. M.; Schwartz, J. C.; Stark, H.; Schunack, W. *Eur. J. Pharm. Sci.* **2002**, *15*, 367.

(14) Break, P.; Musick, T. J.; Chen, C. W. *J. Am. Chem. Soc.* **1988**, *110*, 3538.