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Non-symmetric liquid crystal dimers based on 1,3,4-oxadiazole derivatives: synthesis, photoluminescence and liquid crystal behaviour

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Non-symmetric liquid crystal dimers based on 1,3,4-oxadiazole derivatives: synthesis, photoluminescence and liquid crystal behaviour

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A series of non-symmetric liquid crystal compounds consisting of two different semi-rigid anisometric cores, namely 1,3,4-oxidiazole and biphenyl units, and two short terminal groups, have been synthesised in good yield. It has been shown by polarising optical microscopy and differential scanning calorimetry that all these compounds display liquid crystalline behaviour, with nematic and/or smectic A mesophases. The nature of the mesophases is dependent on the electronic properties of the terminal groups. In methylene chloride solution all the compounds displayed a room temperature emission with λ_{max} at 358–396 nm and quantum yields of 0.29–0.56. The effect of the terminal groups on the mesomorphic and photoluminescent properties is briefly discussed in the context of their electronic characteristics.

Keywords: liquid crystal dimer; photoluminescence; 1,3,4-oxadiazole; synthesis

1. Introduction

Liquid crystal compounds may be composed of molecules containing two mesogenic groups linked by a flexible spacer. Symmetrical liquid crystalline dimers contain two identical mesogenic units, whereas their non-symmetrical analogues have two different mesogenic groups [1–4]. Initial interest in these materials has stemmed from their ability to act as model compounds for semi-flexible main-chain liquid crystal polymers, but they are now of fundamental interest in their own right since their behaviour is significantly different to that of conventional liquid crystals of low molar mass [5–14].

In recent years mesogenic 1,3,4-oxadiazole derivatives have been extensively investigated, both within our own research group [15–22] and by others [23–28], since this type of compound may exhibit tunable liquid crystalline properties with a high quantum yield of luminescence, together with good thermal stability and electron transport properties. In particular, oxadiazole-based compounds have attracted considerable interest on account of their potential to adopt a biaxial nematic phase [29, 30]. Studies based on 1,3,4-oxadiazole-based liquid crystal dimers have, however, been relatively scarce.

Sato and Ujiie [31] reported the first series of LC dimers composed of 2,5-diphenyl-1,3,4-oxadiazole derivatives, containing a range of substituted groups linked by an octamethylenedioxy spacer. They found that the liquid crystalline properties of these compounds were determined by the terminal groups. All the compounds with electron-withdrawing groups exhibited enantiotropic nematic phases, whereas those with electron-donating groups were not liquid crystalline. In contrast, Srivastava *et al.* [32] have recently reported a further series of 1,3,4-oxadiazole-based dimers containing two identical dodecyloxy end-groups and an alkoxy spacer of varying chain length. Although all these compounds displayed blue fluorescence, both in solution and in the solid phase, most showed no liquid crystalline behaviour. In contrast to liquid crystal symmetrical dimers, there is a much wider choice in the design and synthesis of non-symmetric compounds [33, 34]. To the best of our knowledge, however, there have been no examples of non-symmetric 1,3,4-oxadiazole-based liquid crystal compounds reported in the literature.

The biphenyl group is another important structural component used to construct liquid crystalline compounds. These include, for example, the alkoxycyanobiphenyls, which have been studied extensively and are used in twisted and super-twisted nematic display devices due to their high dielectric anisotropy and birefraction, low melting point and low viscosity coefficients [35–39]. In addition, liquid crystal dimers based on biphenyl moieties have also been extensively studied [1, 40].

In the present study we have attempted to combine the advantages associated with 1,3,4-oxadiazole and biphenyl liquid crystal structures, and we are able to report a novel series of non-symmetric liquid crystal compounds. These comprise two different semi-rigid anisometric units connected via a decamethylenedioxy spacer, in which one of the mesogenic moities is a

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2,5-diphenyl-1,3,4-oxadiazole unit and the other a biphenyl group. The liquid crystal properties of these compounds have been investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC). Their electronic UV–Vis absorption and photoluminescence behaviour has also been investigated.

2. Results and discussion

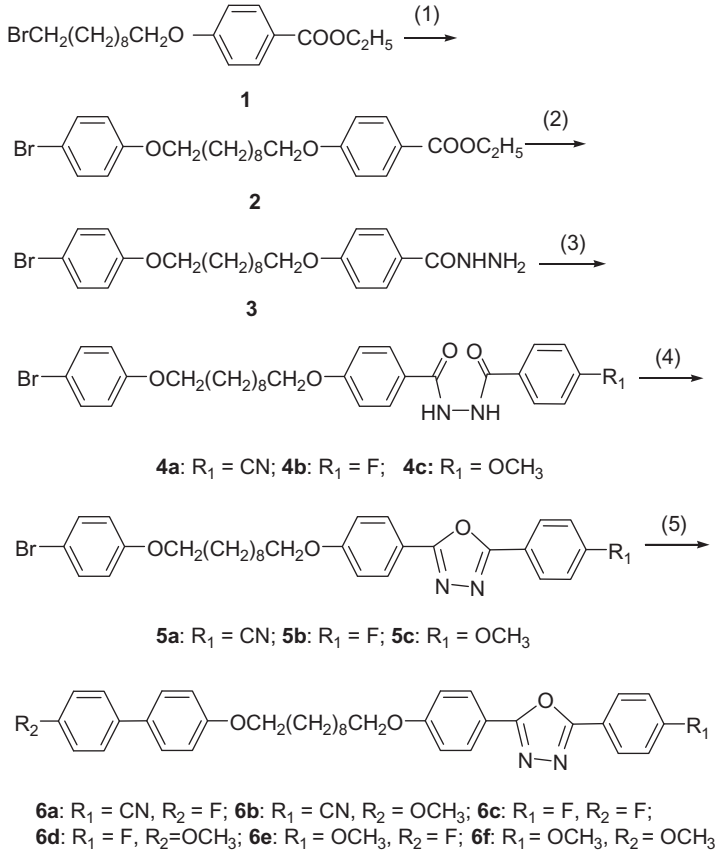
2.1 Synthesis

The synthetic route employed is illustrated in Scheme 1, including the reaction conditions for the target compounds. Following typical procedures reported in the literature [41] the intermediate 1,3,4-oxadiazole derivatives, **5a**–**5c**, were obtained in good yield (64–68%). The final products were also produced in high yield (90–92%), by the reaction of the corresponding 1,3,4-oxadiazole intermediate with a *para*-substituted phenylboronic acid, using the standard Suzuki cross-coupling reaction procedure [42]. The target compounds were each characterised by proton nuclear magnetic resonance (^{1}H NMR), ^{13}C NMR and high-resolution mass spectroscopy (HRMS).

2.2 Liquid crystalline behaviour

The thermotropic liquid crystalline behaviour of the non-symmetric 1,3,4-oxadiazole compounds, **6a**–**6f**, was studied using POM and DSC. The phase transition temperatures observed using thermal microscopy were in reasonable agreement with the corresponding DSC thermograms. The mesomorphism observed is presented in Table 1. All the target compounds demonstrated nematic behaviour, and in addition **6b** and **6c** showed a smectic A mesophase. The nematic phase exhibited a characteristic Schlieren texture with two- and four-brush singularities and typical nematic droplets, while the smectic A phase was identified by the presence of focal–conic and polygonal textures. Typical POM images are illustrated in Figure 1.

As is seen in Table 1, **6a** exhibited an enantiotropic nematic phase, whereas **6b** showed an enantiotropic nematic phase in addition to a monotropic smectic A phase. In contrast, the other compounds, **6c**–**6f**, all



Scheme 1. Reagents and conditions: (1) K_2CO_3, acetone, reflux, 24 h; (2) methanol, hydrazine (80%), reflux; (3) *para*-substituted benzoyl chloride derivative, pyridine, 70°C, 1 h; (4) $POCl_3$, 130°C, 8 h; (5) 4-fluorophenylboronic acid or 4-methoxyphenylboronic acid, $PdCl_2(PPh_3)_2$, K_2CO_3, dioxane/water = 3/1, reflux 3 h.

Table 1. Transition temperatures and enthalpy changes for compounds **6a–6f** during the second heating and first cooling cycles.

Compound	Phase transition[a] T (°C) (ΔH kJ mol^{-1})
6a (R_1 = CN, R_2 = F)	Cr 141.0 (34.7) N 152.2 (1.8) I
	I 150.8 (–2.5) N 123.8 (–35.3) Cr
6b (R_1 = CN, R_2 = OCH_3)	Cr_1 133.8 (10.0) Cr_2 161.2 (43.2) N 176.1 (2.9) I
	I 174.0 (–4.2) N 140.1 (–0.7) SmA 120.4 (–47.2) Cr_3
6c (R_1 = F, R_2 = F)	Cr 141.0 (55.8) I
6d (R_1 = F, R_2 = OCH_3)	I 131.8 (–4.6) N 112.3 [b] SmA 109.2 (–43.9) Cr
	Cr 168.5 (64.8) I
6e (R_1 = OCH_3, R_2 = F)	I 158.5 (–3.7) N 144.5 (–40.8) Cr
	Cr 141.5 (65.8) I
6f (R_1 = OCH_3, R_2 = OCH_3)	I 137.4 (–3.7) N 83.2 (–48.7) Cr
	Cr_1 171.5 (86.4) I
	I 164.7 (–4.3) N 114.0 (–57.7)[c] Cr_2 112.8 Cr_3

Notes: [a]Cr_n = crystal phase (*n*th); SmA = smectic A phase; N = nematic phase; I = isotropic liquid;
[b]Not seen by DSC;
[c]Total enthalpy of the nematic to Cr_2 and Cr_2 to Cr_3 transitions.

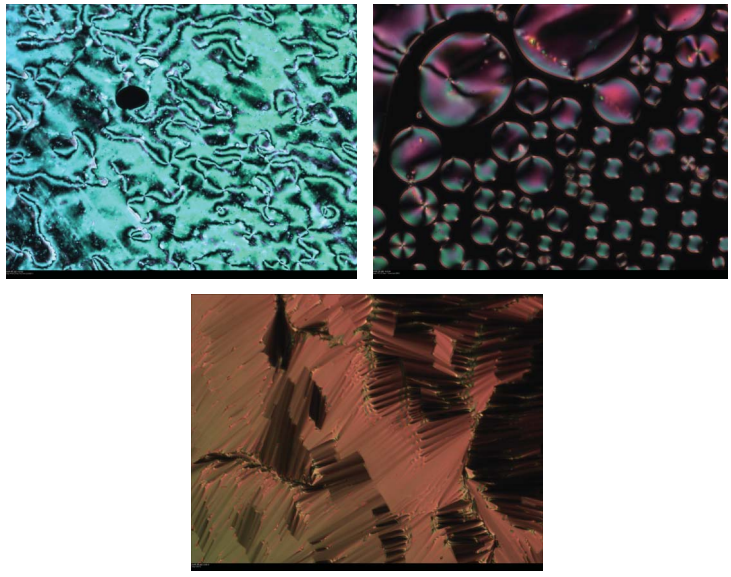


Figure 1. Polarising optical photomicrographs (200×) of: (1) the Schlieren nematic texture of **6a** at 146.8°C during cooling; (2) the nematic droplets of **6b** at 177.2°C during cooling; and (3) the focal–conic texture of the smectic A mesophase of **6b** at 135.0°C during cooling (colour version online).

displayed only a monotropic nematic phase, except that on cooling the nematic melt of **6c**, a monotropic smectic A phase with a very narrow temperature range (*ca*. 3.1°C) was also observed under POM. The only structural difference between compounds **6a**–**6f** lies in their different terminal groups, and it therefore follows that the difference in their liquid crystalline behaviour must also be attributable to these terminal groups. Compounds **6a** and **6b**, having a strongly polar terminal cyano group, tend to form more stable mesophases. The reason for this is possibly that compounds with a terminal cyano group may form a more conjugated structure with the mesogenic core, giving a larger dipole across the molecular axis, and this is believed to play an important role in stabilising the molecular orientation essential for the generation of mesophases [43]. It is interesting to note that compounds **6d** and **6e** are isomers, and the differences in their melting points and mesomorphic temperature ranges therefore indicates that the position of the terminal groups may also have an effect on liquid crystalline behaviour. Compared to conventional symmetrical biphenyl liquid crystal dimers [1], a characteristic of these non-symmetric compounds is the rather

low value of their entropy change associated with the clearing transition, which may be related to the structure of the 1,3,4-oxadiazole unit. However, the precise reason is at present not yet clear. Similar results have also been observed in chlolesteryl-based non-symmetric compounds [34] and in other liquid crystal dimers containing branched terminal chains [45]. The increased biaxiality of the cholesteryl-based group or the branched terminal chains has been thought to be responsible for the low clearing entropies.

2.3 UV–Vis absorption and emission spectroscopy

The UV–Vis absorption and photoluminescence of **6a**, **6b**, **6d** and **6e** in dichloromethane are depicted in Figure 2, and the photophysical data are summarised in Table 2. Similar absorption patterns were observed within these compounds. They all exhibited a strong absorption band at 372–377 nm and a relatively weak absorption band at 248–249 nm. The absorption bands of lowest energy shown by the cyano-substituted compounds, **6a** and **6b**, showed a slight red shift (*ca.* 3–5 nm), as a result of their longer conjugated structure compared with **6d** and **6e**. In solution in dichloromethane all the compounds displayed an intense blue emission at 358–396 nm, with quantum yields in the range 29–56%, on excitation at room temperature at the absorption maximum. As expected, the cyano-terminated compounds had the longest emission wavelength, which may be due to elongated conjugation of the cyano group in association with the mesogenic core. It is interesting that due to their isomeric structure, the UV–Vis absorption and emission spectroscopy of **6d** is quite similar to that of **6e**. On the other hand, they have different quantum yields, which may be attributed to the different location of the terminal groups on the mesogenic cores, but the exact reason is not clear.

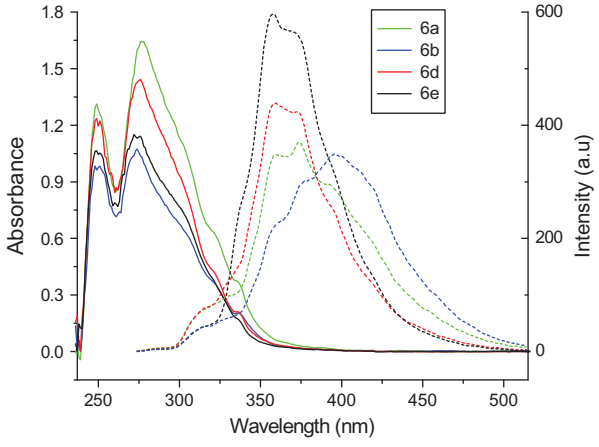


Figure 2. Normalised UV–Vis absorption and emission spectra of **6a**, **6b**, **6d** and **6e** in CH_2Cl_2 at 298K (concentration 5×10^{-6} mol dm^{-3}) (colour version online).

3. Conclusions

The synthesis, mesomorphism and photoluminescence of a novel series of non-symmetric liquid crystal compounds in which the 1,3,4-oxidiazole and biphenyl units are linked by a flexible decylene spacer are described. All the compounds studied exhibited liquid crystalline behaviour, with either enantiotropic or monotropic nematic and smectic A mesophases, and displayed blue fluorescence with λ_{max} in the range 358–396 nm and quantum yields of 0.29–0.56. The mesomorphic and photoluminescence properties are seen to be strongly influenced by the electronic nature of the terminal groups.

4. Experimental

4.1 Equipment and materials

Solution ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer and the chemical shifts quoted in parts per million (ppm) relative to tetramethylsilane as internal standard. Proton decoupled ^{13}C NMR spectra were recorded at 101 MHz on a similar spectrometer. HRMS results were obtained using a Varian QFT–ESI mass spectrometer. Melting points were determined with an X–4 melting point apparatus (Beijing Taike Instrument Co. Ltd.), the thermometer being uncorrected. The liquid crystalline behaviour of all the compounds was studied by POM (Olympus S BX51, equipped with a heating stage). Thermal properties of the bulk materials were studied using a Netsch DSC–204 calorimeter, at a heating and cooling rate of 10°C min^{-1}, precalibrated against an indium standard (156.6°C, 3.3 kJ mol^{-1}). UV–Vis spectra were recorded on a Cary 300 spectrophotometer, and steady-state emission spectra were recorded on the Varian spectrophotometer. The emission quantum yields were determined using the method of Demas and Crosby, with quinine sulphate in degassed 0.1 N sulphuric acid as reference standard ($\Phi = 0.546$) [47].

Ethyl 4-(10-bromodecyloxy)benzoate (**1**) was prepared by the method of Xu *et al*. [48]. Dichloromethane, used for photophysical studies, was washed in turn with concentrated sulphuric acid, 10% sodium bicarbonate and water, dried over calcium chloride, and finally distilled from calcium hydride. All other chemicals and solvents were available commercially and were used as received.

Table 2. UV–Vis absorption and emission data for **6a**, **6b**, **6d** and **6e** in CH_2Cl_2 (concentration = 5×10^{-6} M).

Compound	λ_{abs} (nm) (ε $dm^{-3}mol^{-1}cm^{-1}$)	λ_{em} (nm)[a]	Φ[b]
6a (R_1 = CN, R_2 = F)	249 (2.62×10^5), 277 (3.29×10^5)	374	0.30
6b (R_1 = CN, R_2 = OCH_3)	248 (1.97×10^5), 276 (2.88×10^5)	396	0.42
6d (R_1 = F, R_2 = OCH_3)	249 (2.47×10^5), 273 (2.14×10^5)	359	0.29
6e (R_1 = OCH_3, R_2 = F)	248 (2.13×10^5), 272 (2.30×10^5)	358	0.56

Notes: [a]Excited at absorption maxima;
[b]Determined using quinine sulphate ($\Phi = 0.546$) in 0.1 N H_2SO_4 as standard.

4.2 Synthesis of 4-[10-(4-bromphenoxy)-decyloxy]-benzoic acid ethyl ester (2)

A mixture of 16.2 g (0.042 mol) of compound **1**, 27.6 g (0.200 mol) of potassium carbonate (previously dried under vacuum at 80°C for 12 h) and 8.7 g (0.050 mol) of 4-bromophenol in 100 ml of acetone was refluxed for 24 h. After cooling to room temperature, the solid material was removed by filtration and washed in turn with 100 ml of acetone and 100 ml of chloroform. After removal of the solvent from the combined filtrate, the crude product was dissolved in 100 ml of chloroform. The solution was washed with aqueous NaOH and brine and dried over anhydrous magnesium sulphate, the solvent being removed in a rotary evaporator. The crude solid was washed with distilled water and recrystallised from chloroform/methanol to give the product, **2,** as a white solid.

Yield 56.6%, m.p. 113–114°C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.98 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 7.9 Hz, 2H), 6.77 (d, J = 7.9 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.78 (m, 4H), 1.46–1.33 (m, 15H).

4.3 Synthesis of 4-[10-(4-bromophenoxy)-decyloxy]-benzoic acid hydrazide (3)

A mixture of 11.0 g (23 mmol) of **2** and an excess of hydrazine hydrate in 150 ml of methanol was refluxed for 48 h. The reaction mixture was cooled to room temperature and the precipitate filtered off, washed with water and recrystallised from ethanol, giving compound **3** as a white solid.

Yield 92.5%, m.p. 116–117°C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.69 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.24 (s, Br, 1H), 6.92 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 4.07 (s, Br, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.77 (m, 4H), 1.53–1.26 (m, 12H).

4.4 General procedure for synthesis of Compounds 5

Into a round-bottomed flask (100 mL) were added a *para*-substituted benzoic acid derivative (5 mmol) and thionyl chloride ($SOCl_2$; 10 mL), and the mixture refluxed for 5 h to form the corresponding benzoyl chloride derivative. Excess $SOCl_2$ was removed by vacuum distillation, and the hydrazide **3** (2.3 g, 5 mmol) in pyridine (15 mL) was added dropwise to the benzoyl chloride derivative. The reaction mixture was stirred at room temperature for 2 h and then a further 1 h at 70°C. The reaction mixture was cooled to room temperature and poured into distilled water (50 mL). The white precipitate was filtered off, washed with water and dried to give the raw hydrazides, **4a–4c**, which were used directly in the next step without further purification. The relevant compound **4** was dissolved in phosphoryl chloride ($POCl_3$; 18 ml), and the mixture gently refluxed for 8 h under nitrogen. The excess $POCl_3$ was removed under reduced pressure and the residue purified by silica gel column chromatography using dichloromethane/ethyl acetate (v/v = 20/1) as eluent.

4.4.1 2-(4-(10-(4-bromophenyloxy)decyloxy) phenyl)-5-(4-cyanophenyl)-1,3,4-oxadiazole, **5a**

White solid, yield 66%, m.p. 131–132°C.

^{1}H NMR (400 MHz, *CDCl$_3$*, δ, ppm): 8.25 (d, J = 8.3 Hz, 2H), 8.07 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.5Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.86–1.72 (m, 4H), 1.53–1.29 (m, 12H).

High-resolution mass spectra (HRMS) (Electrospray ionisation (ESI)). Calculated for $C_{31}H_{32}BrN_3O_3$: 573.16. Found: 574.17 ($[M+H]^+$).

4.4.2 2-(4-(10-(4-bromophenyloxy)decyloxy) phenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole, **5b**

White solid, yield 68%, m.p. 105–106°C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 7.35 (d,

$J = 8.9$ Hz, 2H), 7.22 (t, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.9$ Hz, 2H), 4.04 (t, $J = 6.5$ Hz, 2H), 3.91 (t, $J = 6.5$ Hz, 2H), 1.87–1.72 (m, 4H), 1.53–1.29 (m, 12H).

HRMS (ESI): Calculated for $C_{30}H_{32}Br\ FN_2O_3$: 566.1580. Found: 567.11657 ($[M + H]^+$).

4.4.3 2-(4-(10-(4-bromophenyloxy)decyloxy) phenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole, **5c**

White solid, yield 64%, m.p. 120–121°C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.06 (t, $J = 7.6$ Hz, 4H), 7.36 (d, $J = 8.6$ Hz, 2H), 7.02 (t, $J = 7.6$ Hz, 4H), 6.77 (d, $J = 8.6$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 2H), 3.95–3.87 (m, 5H), 1.87–1.72 (m, 4H), 1.53–1.29 (m, 12H).

HRMS (ESI): Calculated for $C_{31}H_{35}Br\ N_2O_4$: 578.1780. Found: 579.1858 ($[M + H]^+$).

4.5 General procedure for synthesis of Compounds 6

Into a round-bottomed flask (100 mL) were added the relevant Compound **5** (0.25 mmol), benzeneboronic acid (0.30 mmol), potassium carbonate (1.25 mmol) and dichloro-bis-(triphenylphosphine) palladium(II) ($PdCl_2(PPh_3)_2$; 5 mg) as catalyst, in solution in a mixture of dioxane (30 mL) and water (10 mL). The mixture was refluxed for 1 h under nitrogen. The reaction mixture was evaporated *in vacuo*, and the solid residue extracted twice with chloroform (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography using chloroform/ethyl acetate (v/v = 20/1) as eluent.

4.5.1 2-(4-cyanophenyl)-5-(4-(10-(4′-fluorobiphenyl-4-yloxy)decyloxy)phenyl)-1,3,4-oxadiazole, **6a**

White solid, yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.17 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 8.6$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.42 (dd, $J = 8.4$, 5.4 Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 2H), 3.92 (t, $J = 6.5$ Hz, 2H), 1.79–1.70 (m, 4H), 1.45–1.17 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.33, 162.21, 161.41 ($J = 58$ Hz), 159.77, 157.62, 135.91 ($J = 11.6$ Hz), 131.78, 127.85, 127.54, 127.46, 127.08 ($J = 31.6$ Hz), 114.56, 114.35, 114.06, 113.75, 67.28, 67.01, 28.44, 28.33, 28.30, 28.24, 28.06, 25.02, 24.94.

HRMS (ESI): Calculated for $C_{37}H_{36}\ FN_3O_3$: 589.2741. Found: 590.4648 ($[M + H]^+$).

4.5.2 2-(4-cyanophenyl)-5-(4-(10-(4′-methoxybiphenyl-4-yloxy)decyloxy) phenyl)-1,3,4-oxadiazole, **6b**

White solid, yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.16 (d, $J = 8.3$ Hz, 2H), 7.99 (d, $J = 8.7$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 4H), 6.96 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 4H), 3.97 (t, $J = 6.5$ Hz, 2H), 3.91 (t, $J = 6.5$ Hz, 2H), 3.76 (s, 3H), 1.80–1.67 (m, 4H), 1.28–1.18 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.39, 161.53, 161.37, 157.63, 157.22, 132.47, 132.23, 131.82, 127.88, 126.95, 126.65, 126.17, 116.96, 114.49, 114.10, 113.87, 113.71, 113.12, 67.31, 67.02, 54.31, 28.68, 28.44, 28.33, 28.29, 28.07, 25.03, 24.94.

HRMS (ESI): Calculated for $C_{38}H_{39}N_3O_4$: 601.2940. Found: 602.3017 ($[M + H]^+$).

4.5.3 2-(4-(10-(4′-fluorobiphenyl-4-yloxy)decyloxy) phenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole, **6c**

White solid, yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.12 (dd, $J = 8.8$, 5.4 Hz, 2H), 8.04 (d, $J = 8.8$ Hz, 2H), 7.21 (t, $J = 8.6$ Hz, 2H), 7.09 (t, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.7$ Hz, 2H), 7.48 (dd, $J = 8.7$, 5.4 Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 4.03 (t, $J = 6.5$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 1.81–1.66 (m, 4H), 1.46 –1.36 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 165.94, 164.65, 163.37 ($J = 44.4$ Hz), 162.03, 160.85, 158.68, 137.00 ($J = 12.4$ Hz), 132.61, 129.08 ($J = 34.8$ Hz), 128.68, 128.18 ($J = 31.2$ Hz), 127.99, 120.48 ($J = 12.0$ Hz), 116.50, 116.27, 116.04, 115.63, 115.42, 115.01, 114.81, 68.28, 68.08, 29.49, 29.38, 29.36, 29.30, 29.13, 26.07, 26.00.

HRMS (ESI): Calculated for $C_{36}H_{36}F_2\ N_2O_3$: 582.2694. Found: 583.2764 ($[M + H]^+$).

4.5.4 2-(4-fluorophenyl)-5-(4-(10-(4′-methoxybiphenyl-4-yloxy)decyloxy) phenyl)-1,3,4-oxadiazole, **6d**

White solid, yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.13 (dd, $J = 8.4$, 5.4 Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.0$Hz, 2H), 7.46 (d, $J = 8.0$Hz, 2H), 7.22 (t, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.8$Hz, 2H), 6.94 (d, $J = 8.8$Hz, 2H), 4.04

(t, $J = 6.5$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.84 (s, 3H), 1.88–1.74 (m, 4H), 1.48–1.36 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 165.94, 164.66, 163.30, 162.04, 158.68, 158.27, 136.53 ($J = 12.4$ Hz), 135.55, 133.29, 129.08 ($J = 34.8$ Hz), 128.68, 127.69, 116.48, 116.26, 116.07, 115.02, 114.76, 114.16, 68.30, 68.08, 55.34, 29.47, 29.36, 29.33, 29.31, 29.16, 26.06, 25.99.

HRMS (ESI): Calculated for $C_{37}H_{39}FN_2O_4$: 594.2894. Found: 595.2970 ($[M + H]^+$).

4.5.5 2-(4-(10-(4′-fluorobiphenyl-4-yloxy)decyloxy) phenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole, **6e**

White solid, yield 92%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.05 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.49 (dd, $J = 8.6$, 5.6 Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.09 (t, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.88 (s, 3H), 1.86–1.76 (m, 4H), 1.53–1.31 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.09 ($J = 41.2$ Hz), 163.27, 162.17, 161.80, 160.83, 158.67, 137.00 ($J = 12.4$ Hz), 132.58, 128.55, 128.16 ($J = 31.2$ Hz), 127.97, 116.66, 116.36, 115.60, 115.39, 114.93, 114.80, 114.45, 68.23, 68.07, 55.46, 29.48, 29.37, 29.34, 29.28, 29.13, 26.05, 25.99.

HRMS (ESI): Calculated for $C_{37}H_{39}FN_2O_4$: 594.2894. Found: 595.2977 ($[M + H]^+$).

4.5.6 2-(4-(10-(4′-methoxybiphenyl-4-yloxy)decyloxy) phenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole, **6f**

White solid, yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.05 (d, $J = 7.4$ Hz, 4H), 7.47 (d, $J = 7.4$, 4H), 7.02 (d, $J = 7.1$ Hz, 4H), 6.95 (d, $J = 7.1$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 1.86–1.76 (m, 4H), 1.53–1.31 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.18, 164.06, 162.17, 161.82, 158.64, 158.25, 133.54, 133.26, 128.58, 127.69, 116.68, 116.36, 114.97, 114.94, 114.76, 114.74, 114.46, 114.14, 68.25, 68.06, 55.47, 55.35, 29.48, 29.37, 29.34, 29.30, 29.14, 26.06, 25.99.

HRMS (ESI): Calculated for $C_{38}H_{42}N_2O_5$: 606.3094. Found: 607.3173 ($[M + H]^+$).

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References

[1] Imrie, C.T.; Henderson, P.A. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 298–311.
[2] Imrie, C.T. *Liq. Cryst.* **2006**, *33*, 1449–1454.
[3] Imrie, C.T.; Henderson, P.A. *Chem. Soc. Rev.* **2007**, *36*, 2096–2124.
[4] Imrie, C.T.; Henderson, P.A.; Yeap, G.Y. *Liq. Cryst.* **2009**, *36*, 755–777.
[5] Araya, K.; Dunmur, D.A.; Grossel, M.C.; Luckhurst, G.R.; Marchant-Lane, S.E.; Sugimura, A. *J. Mater. Chem*. **2006**, *16*, 4675–4689.
[6] Ferrarini, A.; Greco, C.; Luckhurst, G.R. *J. Mater. Chem.* **2007**, *17*, 1039–1042.
[7] Aziz, N.; Kelly, S.M.; Duffy, W.; Goulding, M. *Liq. Cryst.* **2008**, *35*, 1279–1292.
[8] Srivastava, R.M.; Filho, R.A.W.N.; Schneider, R.; Vieira, A.A.; Gallardo, H. *Liq. Cryst.* **2008**, *35*, 737–742.
[9] Yelamaggad, C.V.; Shashikala, I.S.; Tamilenthi, V.P.; Rao, D.S.S.; Nair, G.G.; Prasad, S.K. *J. Mater. Chem.* **2008**, *18*, 2096–2103.
[10] Toh, C.L.; Xu, J.; Lu, X.; He, C. *Liq. Cryst.* **2008**, *35*, 241–251.
[11] Bai, B.; Wang, H.; Zhang, P.; Qu, S.; Li, F.; Yu, Z.; Long, B.; Li, M. *Liq. Cryst*. **2008**, *35*, 793–798.
[12] Wang, H.; Shao, R.; Zhu, C.; Bai, B.; Gong, C.; Zhang, P.; Li, F.; Li, M.; Clark, N.A. *Liq. Cryst*. **2008**, *35*, 967–974.
[13] Bialecki-Florjanczyk, E.; Sledzinska, I.; Przedmojski, J.; Gorecka, E. *Liq. Cryst*. **2008**, *35*, 401–406.
[14] Bhowmik, P.K.; Han, H.; Nedeltchev, K.; Mandal, H.D.; Jimenez-Hernandez, J.A.; McGannon, P.M.; Lopez, L.; Kang, S.W.; Kumar, S. *Liq. Cryst.* **2009**, *36*, 1389–1399.
[15] Han, J.; Chui, S.S.-Y.; Che, C.-M. *Chem. Asian J.* **2006**, *1*, 814–825.
[16] Han, J.; Wang, J.-Y.; Zhang, F.-Y.; Zhu, L.-R.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst*. **2008**, *35*, 1205–1214.
[17] Han, J.; Zhang, F.-Y.; Chen, Z.; Wang, J.-Y.; Zhu, L.-R.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst*. **2008**, *35*, 1359–1365.
[18] Han, J.; Chang, X.-Y.; Zhu, L.-R.; Wang, J.-B.; Meng, Y.-M.; Chui, S.S.-Y. *Liq. Cryst.* **2008**, *35*, 1379–1394.
[19] Zhu, L.; Yao, F.; Han, J.; Pang, M.; Meng, J. *Liq. Cryst*. **2009**, *36*, 209–213.
[20] Han, J.; Zhang, F.-Y.; Wang, J.-Y.; Wang, Y.-M.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst.* **2009**, *36*, 825–833.
[21] Han, J.; Chang, X.-Y.; Cao, B.-N.; Wang, Q.-C. *Soft Matter* **2009**, *7*, 342–354.
[22] Han, J.; Wang, F.-L.; Zhang, F.-Y.; Zhu, L.-R. *Liq. Cryst.* **2010**, *37*, 1521–1527.
[23] Wen, C.-R.; Wang, Y.-J.; Wang, H.-C.; Sheu, H.-S.; Lee, G.-H.; Lai, C.K. *Chem. Mater.* **2005**, *17*, 1646–1654.

[24] Cristiano, R.; Vieira, A.A.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2006**, *33*, 381–390.
[25] Parra, M.; Hidalgo, P.; Carrasco, E.; Barberá, J.; Silvino, L. *Liq. Cryst.* **2006**, *33*, 875–882.
[26] He, C.F.; Richards, G.J.; Kelly, S.M.; Contoret, A.E.A.; O'Neill, M. *Liq. Cryst.* **2007**, *34*, 1249–1267.
[27] Qu, S.; Chen, X.; Shao, X.; Li, F.; Zhang, H.; Wang, H.; Zhang, P.; Yu, Z.; Wu, K.; Wang, Y.; Li, M. *J. Mater. Chem.* **2008**, *18*, 3954–3964.
[28] Yelamaggad, C.V.; Achalkumar, A.S.; Rao, D.S.S.; Krishna Prasad, S. *J. Org. Chem.* **2009**, *74*, 3168–3171.
[29] Zafiropoulos, N.A.; Lin, W.; Samulski, E.T.; Dingemans, T.J.; Picken, S.J. *Liq. Cryst.* **2009**, *36*, 649–656.
[30] Acharya, B.R.; Primak, A.; Kumar, S. *Phys. Rev. Lett.* **2004**, *92*, 145505.
[31] Sato, M.; Ujiie, S. *Adv. Mater*. **1996**, *8*, 567–569.
[32] Srivastava, R.M.; Filho, R.A.W.N.; Schneider, R.; Vieira, A.A.; Gallardo, H. *Liq. Cryst.* **2008**, *35*, 737–742.
[33] Attard, G.S.; Date, R.W.; Imrie, C.T.; Luckhurst, G.R.; Roskilly, S.J.; Seddon, J.; Taylor, M.L. *Liq. Cryst.* **1994**, *16*, 529–581.
[34] Donaldson, T.; Staesche, H.; Lu, Z.B.; Henderson, P.A.; Achard, M.F.; Imrie, C.T. *Liq. Cryst.* **2010**, *37*, 1097–1110.
[35] Das, M.K.; Paul, S.; Raul, R. *Mol. Cryst. Liq. Cryst.* **1995**, *264*, 89–98.
[36] Hori, K.; Wu, H. *Liq. Cryst.* **1999**, *26*, 37–43.
[37] Hirar, Y.; Babu, S.S.; Praveen, V.K.; Yasuda, T.; Ajayaghosh, A.; Kato, T. *Adv. Mater.* **2009**, *21*, 4029–4033.
[38] Mizoshita, N.; Kato, T. *Adv. Funct. Mater.* **2006**, *16*, 2218–2224.
[39] Sied, M.B.; Diez, S.; Salud, J.; López, D.O.; Cusmin, P.; Tamarit, J.T.; Barrio, M. *J. Phys. Chem. B* **2005**, *109*, 16284–16289.
[40] Bisoyi, H.K.; Kumar, S. *Phase Transitions*, **2006**, *79*, 285–292.
[41] Kim, J.H.; Lee, H. *Synth. Met.* **2004**, *143*, 13–19.
[42] Aldred, M.P.; Eastwood, A.J.; Kelly, S.M.; Vlachos, P.; Contoret, A.E.A.; Farrar, S.R.; Mansoor, B.; O'Neil, M.; Tsoi, W.C. *Chem. Mater.* **2004**, *16*, 4928–4936.
[43] Kumar, S. *Liquid Crystals: Experimental Study of Physical Properties and Phase Transition*; Cambridge University Press: Cambridge, 2001.
[44] Sung, H.-H.; Lin, H.-C. *Liq. Cryst.* **2004**, *31*, 831–841.
[45] Blatch, A.E.; Fletcher, I D.; Luckhurst, G.R. *J. Mater. Chem.* **1997**, *7*, 9–17.
[46] Yeap, G.Y.; Hng, T.C.; Yeap, S.Y.; Gorecka, E.; Ito, M.M.; Ueno, K.; Okamoto, M.; Mahmood, W.A.K.; Imrie, C.T. *Liq. Cryst.* **2009**, *36*, 1431–1441.
[47] Demas, J.N.; Crosby G.A. *J. Phys. Chem.* **1971**, *75*, 991–1024.
[48] Xu, J.; Toh, C.L.; Liu, X.; Wang, S.; He, C.; Lu, X. *Macromolecules*, **2005**, *38*, 1684–1690.