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Effect of polar substituents on the properties of 1,3,4-oxadiazole-based liquid crystalline materials containing asymmetric cores

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A series of 1,3,4-oxadiazole-based liquid crystals bearing different polar substituents (*n*-NPO-*X*, where *X* = Me, OMe, Cl, F, CN, and NO_2) at the phenyl 4-position have been synthesized and characterized. These angular oxadiazole-based liquid crystals, which are composed of asymmetric cores containing naphthalene units, exhibit stable mesogenic properties including the nematic and smectic A phases. With analogous structural design, the transition temperatures, mesomorphic phases, optical properties, and internal quantum efficiencies show strong dependence on the terminal substitution. In general, by increasing the terminal dipoles, the temperature ranges of the mesophases are enhanced, and both the absorption and photoluminescence spectra are shifted to longer wavelengths.

1. Introduction

The design and synthesis of liquid crystals (LCs) containing heterocyclic units have been the subject of much research in recent years [1–6]. Due to greater choices in the design of new mesogenic molecules containing heterocyclic rings, the polarity and geometry of the molecules may be varied by the introduction of hetero-atoms [7, 8]. These factors lead to dramatic changes in the types of mesophase and the phase transition temperatures in heterocyclic liquid crystalline materials.

Dipole–dipole interactions and structural shapes are fundamental elements in the design of liquid crystals [9]. However, the role of polar units in the generation of liquid crystalline phases still needs to be explored in novel heterocyclic systems, because polar substituents are highly variable, and their attaching sites are also adjustable. These benefits allow us to access a wide variety of mesophases simply by changing the polar moieties or their attaching positions.

1,3,4-Oxadiazole-based LC derivatives, which possess asymmetric structures containing the oxadiazole ring in the central position of the mesogenic core, were first proposed by Dimitrowa *et al.* [10]. The introduction of oxadiazole rings can provide not only the lateral dipole from the oxygen and nitrogen atoms, but also the bent shape of the rigid cores. This large lateral dipole leads to the possibility of hexagonal columnar phases when oxadiazole rings are used as central cores [11]. In addition, star-shaped molecules containing 2,5-diphenyloxadiazole units as rigid arms possess a discotic nematic phase [12]. Compounds having both oxadiazole and pyridinium groups may exhibit liquid crystalline properties as well as thermochromic behaviour, with a colour change from yellow at room temperature to bright red in the mesophase [13].

The choice of terminal moieties is crucial in the generation of specific types of liquid crystalline phases. In this study, a series of 1,3,4-oxadiazole-based liquid crystals with different terminal polar units have been synthesized; their liquid crystalline and photoluminescent properties with respect to various terminal polarities have been investigated.

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2. Results and discussion

2.1. *Mesophases and thermal properties*

The series of 1,3,4-oxadiazole-based liquid crystals containing different polar substituents are depicted in figure 1. From previous studies, it is known that 2,5-diphenyl-1,3,4-oxadiazole has an exocylic bond angle ($\sim 134^\circ$) with a 3.86 D dipole moment pointed to the oxygen atom of the oxadiazole [14]. These new oxadiazole-based materials therefore also have large exocylic bond angles and lateral dipole moments.

The phase behaviour of these materials is shown in table 1. The temperature ranges (3.1–62.4°C) of the mesophases are probably influenced by the bent structure of the rigid core, which originates from the

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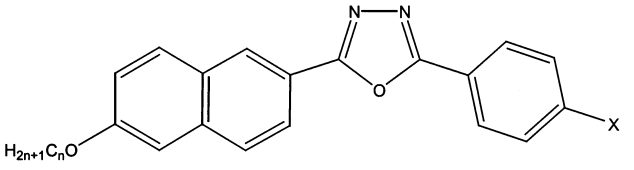


n-NPO-X

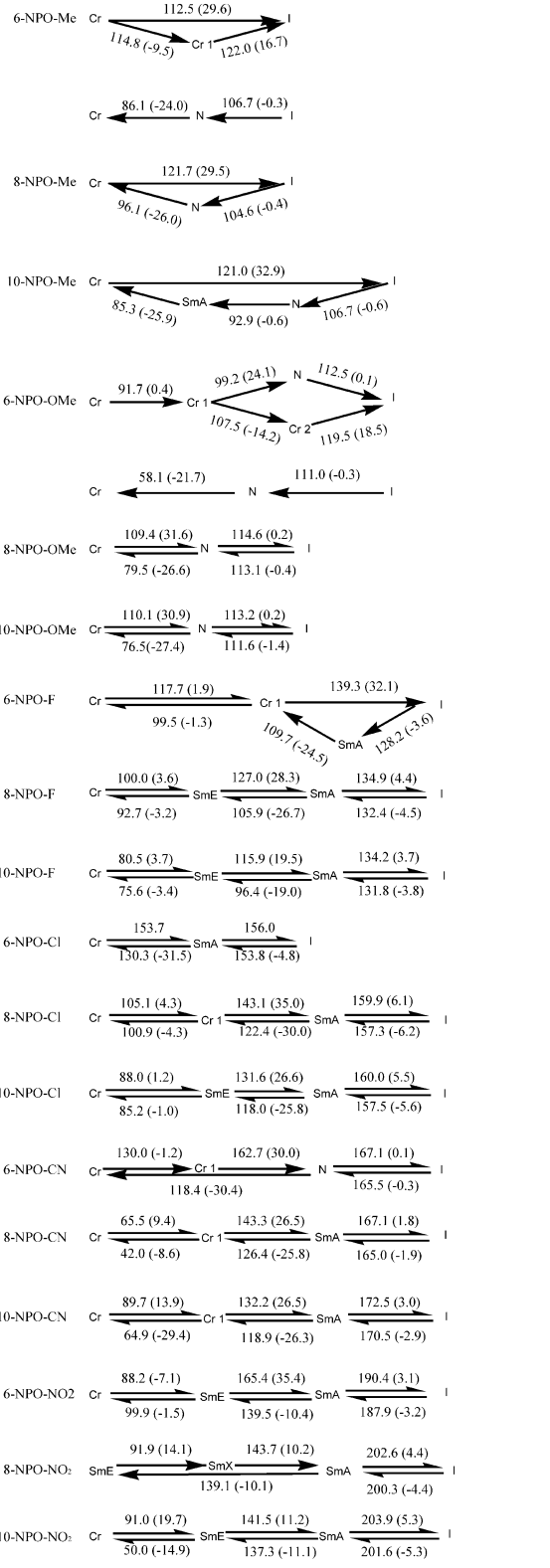
where n = 6, 8, and 10;
and X = Me, OMe, F, Cl, CN, and NO_2

Figure 1. Chemical structures of the synthesized molecules.

non-linear 1,3,4-oxadiazole ring, as well as by the flexible chain lengths and polar terminal groups. All the compounds with electron-donating terminal groups, i.e. *n*-NPO-Me and *n*-NPO-OMe, exhibit the nematic (N) phase characterized by schlieren textures. Methoxy-substituted compounds (NPO-OMe) possess enantiotropic mesophase behaviour; however, methyl-substituted compounds (NPO-Me) display a monotropic nematic phases. Surprisingly, 10-NPO-Me has a focal-conic texture indicating a smectic A (SmA) phase, but 10-NPO-OMe has no SmA phase. This might be explained by cancellation of the opposing dipole moments of the methoxy group and oxadiazole unit. This effect is also evident in that the isotropization temperatures of *n*-NPO-Me are higher than those of analogous *n*-NPO-OMe. As it can be seen in figure 2, 6-NPO-Me and 6-NPO-OMe both recrystallize before reaching their isotropic points. In particular, 6-NPO-OMe enters the N phase at 99.2°C, then part of the domain begins to recrystallize. The N phase becomes isotropic at 112.5°C, and the recrystallized domain melts at 119.5°C. This unusual behaviour has also been observed in glass-forming liquid crystals [15].

These LC materials, incorporating the strongly polar electron-withdrawing terminal groups F, Cl, CN and NO_2, exhibit the SmA phase (except 6-NPO-CN). During cooling in the polarizing optical microscope, 10-NPO-NO_2 shows a typical focal-conic texture of the SmA phase at 150°C, figure 3 (*a*); at 130°C the mesophase then transfers to a paramorphotic arced focal-conic fan texture which is tentatively assigned as the smectic E phase, figure 3 (*b*). In a literature search it was found that an oxadiazole-based material (2,5-diphenyl-1,3,4-oxadiazole, see figure 4) containing a symmetric core, which is similar to 6-NPO-CN of this report, possesses only a crystalline phase [10]. In comparison with the analogous structure containing the symmetric diphenyl core, 6-NPO-CN shows mesomorphic properties owing to the replacement of one phenyl group by a naphthalene unit to generate an asymmetric core. Therefore, our molecular design of

Table 1. Phase behavior of *n*-NPO-*X* derivatives. Transition temperatures (°C) and enthalpies (in parentheses, kJ mol^{-1}) were determined by DSC (10°C min^{-1}).



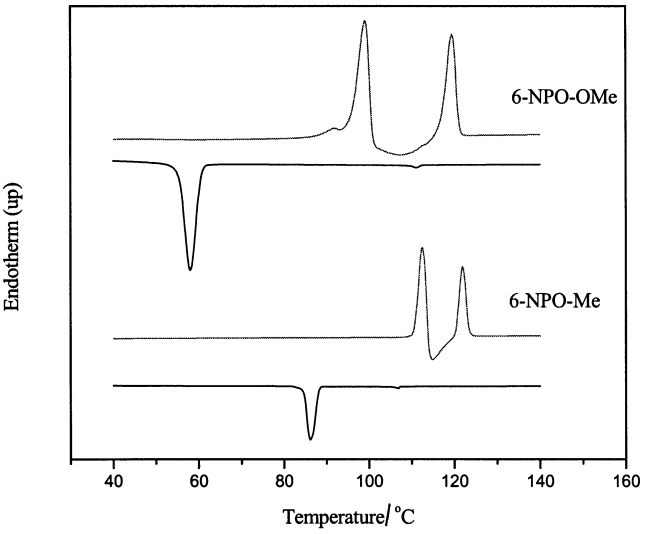


Figure 2. DSC thermograms of 6-NPO-OMe and 6-NPO-Me during first cooling and second heating.

asymmetric cores containing naphthalene units do enhance the occurrence of liquid crystallinity in this study.

Although fluorine has larger electronegativity than chlorine, from the literature [16] the chloro-substituted system (NPO-Cl) actually generates a larger dipole than the fluoro-substituted system (NPO-F) because of the longer bond distance from chlorine to carbon. The angular mesogens carrying different terminal groups indeed influence the mesogenic phases and the transition temperatures in 8-NPO-*X* analogues (see figure 5). Both the melting and liquid crystallization temperatures (on cooling) increase with the increasing terminal dipoles. The clearing temperature and crystallization temperature have a similar tendency, except for the methyl-substituted compound (8-NPO-Me). Another interesting trend is that the mesogenic phase range also

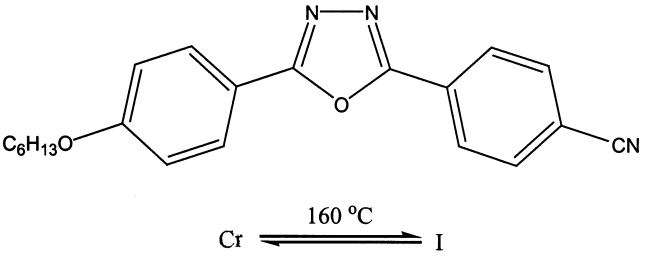


Figure 4. Structure containing a diphenyl symmetric core [10].

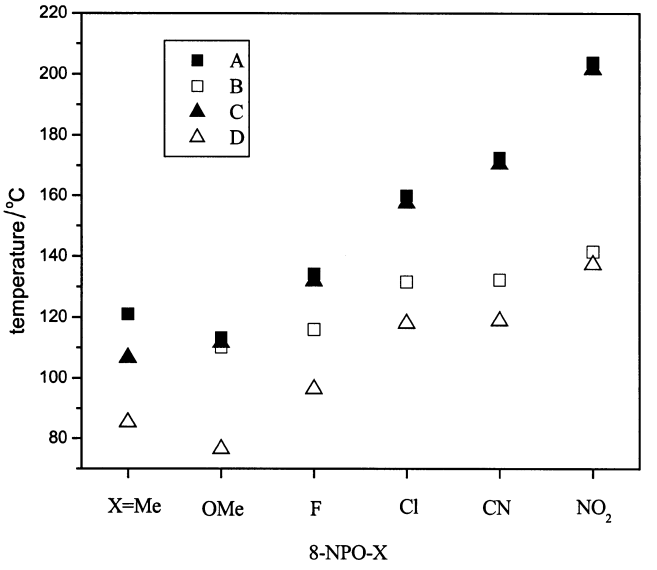
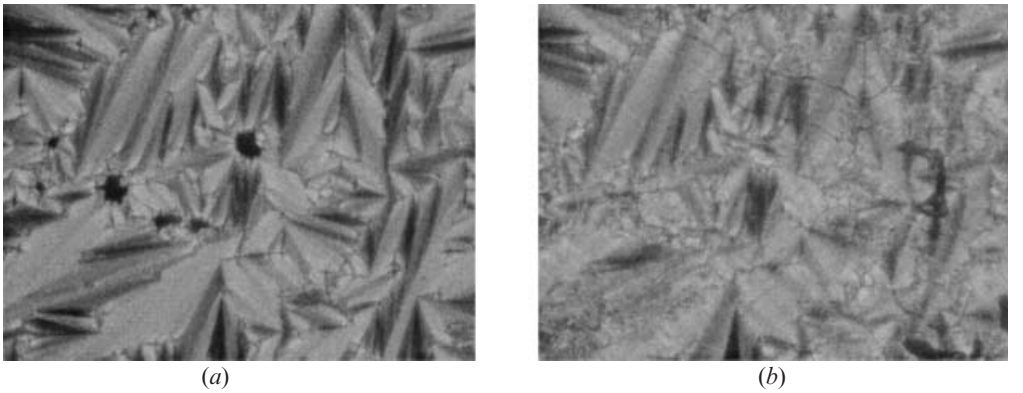


Figure 5. The effect of polar substituents on the transition temperatures (dipole increases from left to right). (A) clearing point, (B) melting point, (C) liquid crystallization temperature (on cooling), (D) crystallization temperature.

increases with increasing terminal dipoles (see figure 6), especially during heating; the mesomorphic temperature ranges from 3.1°C with the methoxy group (8-NPO-OMe)



(*a*) (*b*)

Figure 3. Optical textures of compound 10-NPO-NO_2. (*a*) Focal-conic texture at 150°C (cooling); (*b*) transfers to a paramorphotic arced focal–conic fan texture at 130°C (cooling).

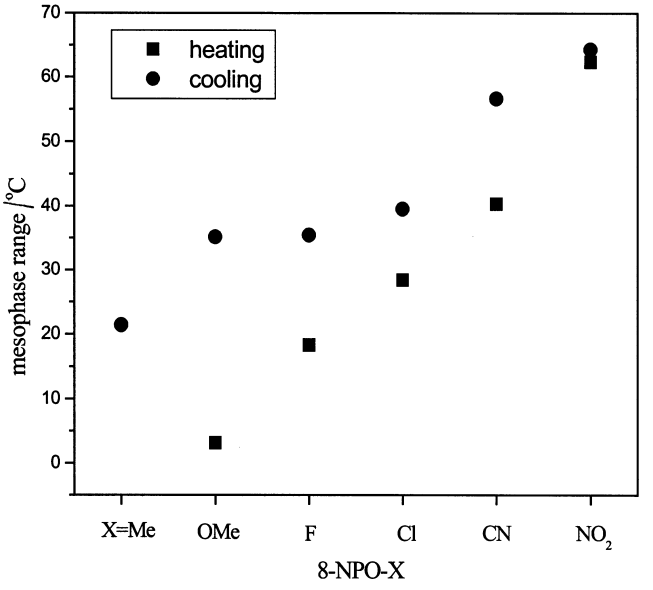


Figure 6. The effect of polar substituents on the mesophase range during heating and cooling cycles (dipole increases from left to right).

up to 62.4°C with the nitro group (8-NPO-NO_2). From this result, it can be seen that the mesogenic phase ranges of these oxadiazole-based structures can be enlarged by increasing the terminal dipoles, and that both the melting and clearing temperatures can also be raised.

The optical texture of nematic liquid crystals is an important diagnostic for the presence of a biaxial phase. It has been proposed that the elastic constants of a biaxial nematic should produce only two-brush ($|S|=1/2$) patterns [17]. In our system, when nematic samples of *n*-NPO-Me and *n*-NPO-OMe are placed between two untreated glass plates, a schlieren texture consisting only of two-brush disclinations is observed; four-brush disclinations ($|S|=1$) are absent (see figure 7). It is reported that bent-shaped or boomerang-shaped materials may be candidates for a biaxial nematic phase (N_b) [18, 19], hence, the mesogenic unit containing 1,3,4-oxadiazole which provides a large exocylic bond angle, may possibly lead to N_b materials.

2.2. *Photoluminescent properties*

The absorption spectra of the synthesized materials *n*-NPO-*X* in solution (chloroform) are depicted in figure 8. Similar absorption patterns between 300 and 400 nm are observed in various substituted derivatives of 8-NPO-*X* (*X* = Me, OMe, F, and Cl). Nevertheless, both the cyano- and nitro-substituted compounds have longer absorption wavelengths. Except for the

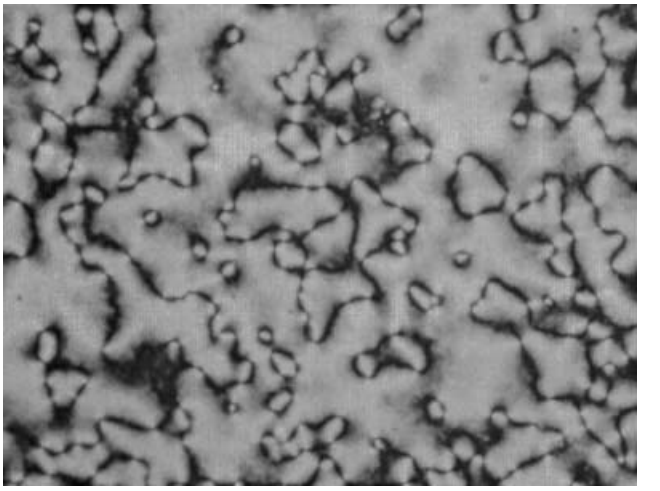


Figure 7. Schlieren texture exhibited by the nematic phase of compound 6-NPO-OMe (sandwiched between two untreated glass plates). Note that only two-brush disclinations, $|S|=1/2$, are observed.

fluoro-substituted compounds (*n*-NPO-F), a general polar substituent effect is observed; i.e. substituted groups with a stronger dipole result in larger red shifts of absorption ($NO_2 > CN > Cl > OMe > Me$). Moreover, the strongest polar substituent effect, resulting in the largest red shift (>30 nm), is observed in the nitro-substituted compound 8-NPO-NO_2. This shift may be due to the electronic effect, which lowers the LUMO level (as in p-doped semiconductors) and reduces the energy gap [20].

Normalized photoluminescence (PL) spectra are shown in figure 9, and peak positions are summarized in table 2. The emission colours of these 8-NPO-*X* derivatives are all in the purple region. The

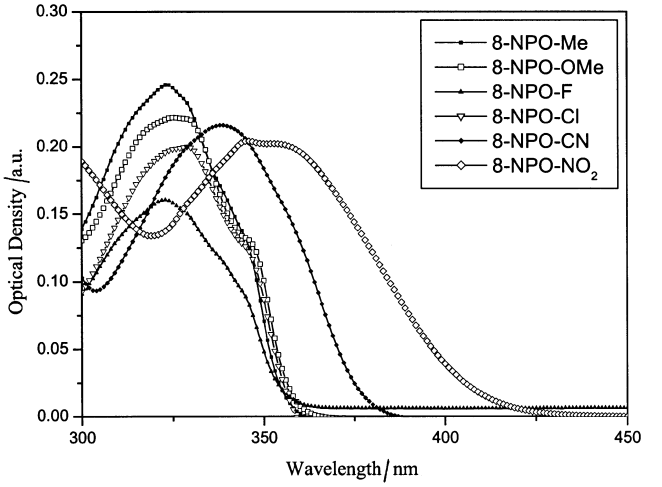


Figure 8. Normalized absorption spectra of 8-NPO-*X* derivatives in solution (chloroform).

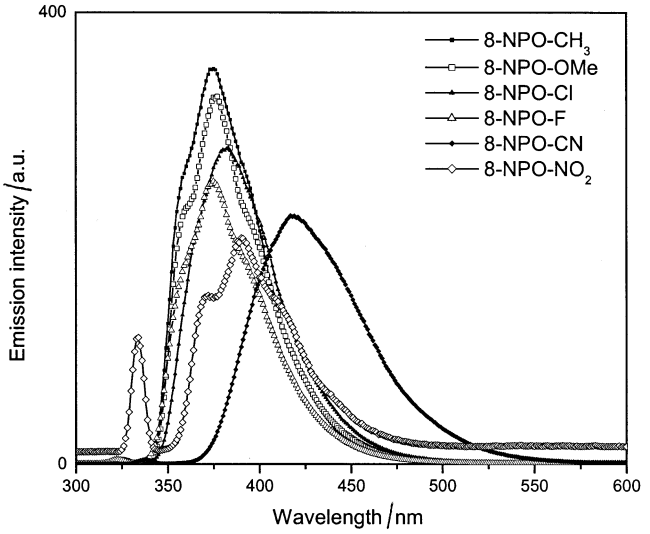


Figure 9. Normalized PL spectra of 8-NPO-*X* derivatives in solution (chloroform).

methyl-substituted compound 8-NPO-Me has the shortest (PL) wavelength, whereas the stronger dipole substituted compounds have longer PL emission wavelengths. The cyano-substituted compound 8-NPO-CN has the longest emission wavelength, which may be due to the elongated conjugation length of the cyano group in conjuction with the mesogenic core. The relative PL quantum yields of these materials are measured in contrast to 8-NPO-Me. The chloro-substituted compound 8-NPO-Cl has the highest quantum yield, while the nitro-substituted compound 8-NPO-NO_2 has the lowest quantum yield. The quenching effect induced by nitro-substitution has also been observed by Wong *et al.* [21], and is due to the photocurrent generated by the nitro-substituent.

The PL dichroic (D_{PL}) behaviour of these materials was also examined. The emission intensity is highest when the polarizer is parallel to the rubbing direction of the aligned cell, and lowest in the direction perpendicular to it. This property yields a PL dichroic ratio $D_{PL} = I_{\|}/I_{\perp}$, where $I_{\|}$ and $I_{\perp}$ are values of the PL intensities parallel and perpendicular to the rubbing direction, respectively [22]. The values of D_{PL} have been estimated from 1.4 to 3.4 at the temperatures where the highest D_{PL} values are seen (table 3). These results indicate that the conjugated cores are aligned predominantly along the rubbing direction. 10-NPO-Me possesses the largest $D_{PL} = 3.4$ at 100°C, which means that this material has the highest order parameter among these oxadiazole derivatives.

Table 2. Absorption and photoluminescence spectra of 8-NPO derivatives.

Compound	Absorption peak/nm	Emission PL peak/nm	Relative quantum yield
8-NPO-Me	323	374	1
8-NPO-OMe	325	377	1.05
8-NPO-F	323	375	0.95
8-NPO-Cl	329	383	1.3
8-NPO-CN	338	417	1.05
8-NPO-NO_2	346	390	0.05

3. Summary

A new class of mesomorphic molecules containing 1,3,4-oxadiazole-based mesogenic cores has been prepared. These bent-shaped molecules exhibit nematic and smectic A phases. In general, the mesogenic phases and optical properties of these oxadiazole-based LC materials are strongly influenced by their terminal functional groups. By increasing the terminal dipoles, the mesophase ranges are enhanced, and both the absorption and photoluminescence spectra are shifted toward longer wavelengths.

4. Experimental

4.1. *Characterization*

Chemicals and solvents were reagent grades and purchased from Aldrich, ARCROS, TCI and Lancaster Chemical Co. Pyridine and *N*-methyl-2-pyrrolidone (NMP) were distilled before use to remove water. Other chemicals were used without further purification. ^{1}H NMR spectra were recorded on a Varian unity 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. Elemental analyses were performed on a Heraeus CHN-OS RAPID elemental analyzer. High resolution electron impact mass data were obtained on a Finnigan-MAT-95XL. Mesophase textures were studied using a polarizing optical microscope (Leica

Table 3. PL dichroic ratio (D_{PL}) and order parameter of *n*-NPO-*X* in various conditions.

Compound	Temperature/°C	Maximum PL dichroic ratio[a]	Order parameter[b]
10-NPO-Me	100	3.4	0.44
6-NPO-OMe	85	1.8	0.21
10-NPO-F	110	1.9	0.23
10-NPO-Cl	150	1.4	0.11
10-NPO-CN	130	1.7	0.19
10-NPO-NO_2	150	1.6	0.17

[a]The PL dichroic ratio ($D_{PL} = I_{\|}/I_{\perp}$) is obtained from the photoluminescence spectra (using the highest intensities of $I_{\|}$ and $I_{\perp}$) at the temperature which gives the highest value.
[b]Order parameter $= (I_{\|} - I_{\perp})/(I_{\|} + 2I_{\perp})$.

DMLP) equipped with a hot stage. Transition temperatures were determined by differential scanning calorimetry (Perkin Elmer Pyris 7) with heating and cooling rates of $10^{\circ}C\,min^{-1}$.

4.2. *Synthesis*

The synthetic route to the 1,3,4-oxadiazole-based liquid crystalline materials of this study is shown in the scheme. 6-Hydroxynaphthalene-2-carboxylic acid methyl ester (**1**) was prepared using a modification of the procedure described by Güller *et al.* [23]. Compounds 2a–c were obtained by *o*-alkylation of compound **1** with appropriate *n*-alkyl bromides, according to a procedure reported previously [24]. The synthetic procedures and chemical analyses of each product are described sequentially below.

4.2.1. *6-Hexyloxynaphthalene-2-carboxylic acid hydrazide (**3a**)*

A mixture of 2.23 g (7.78 mmol) of compound **1** and 3.90 g (77.8 mmol) of hydrazine monohydrate was dissolved in methanol, and the solution heated under reflux for 24 h. After cooling, the reaction mixture was poured into water and the separated solid recrystallized from methanol. yield: 83%. ^{1}H NMR (ppm, DMSO-d_6): 0.88 (t, $-CH_3$, 3H), 1.22–1.79 (m, $-CH_2$, 8H), 4.09 (t, $-OCH_2$, 2H), 4.50 (s, $-NH_2$, 2H), 7.18 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.34 (s, $-C_{10}H_6$, 1H), 7.80–7.90 (m, $-C_{10}H_6$, 3H), 8.33 (s, $-C_{10}H_6$, 1H), 9.81 (s, –NH, 1H).

4.2.2. *6-Octyloxynaphthalene-2-carboxylic acid hydrazide (**3b**)*

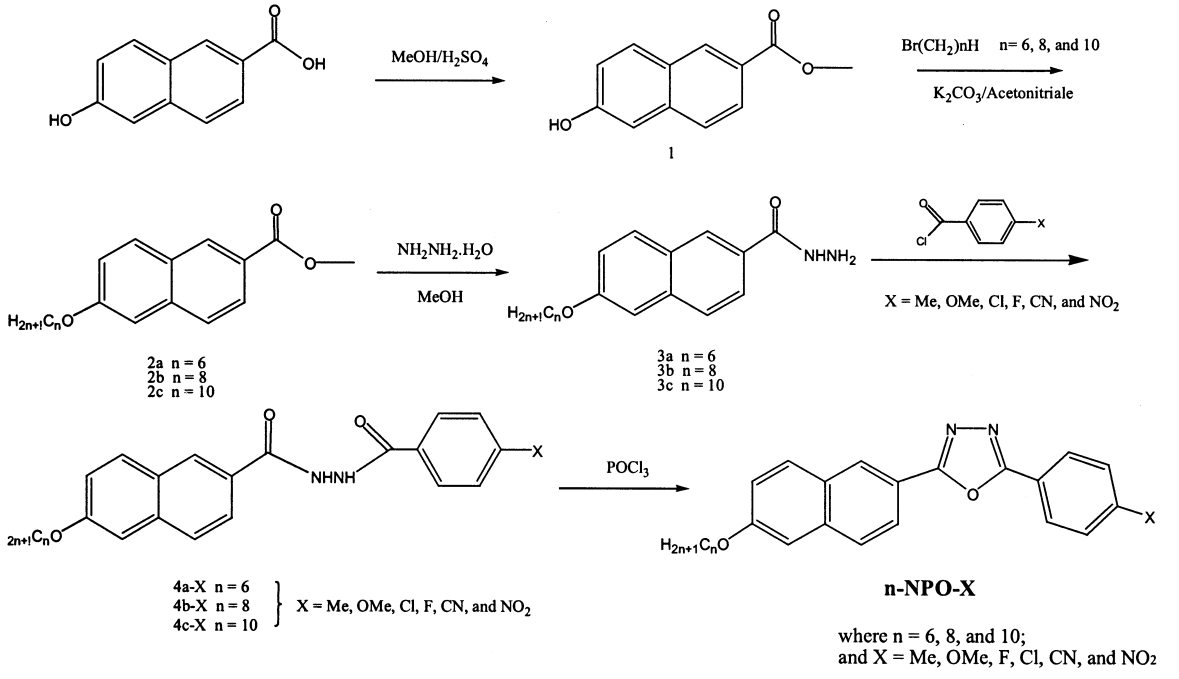
Yield: 79%. ^{1}H NMR (ppm, DMSO-d_6): 0.85 (t, $-CH_3$, 3H), 1.25–1.79 (m, $-CH_2$, 12H), 4.08 (t, $-OCH_2$, 2H), 4.52 (s, $-NH_2$, 2H), 7.17 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.33 (s, $-C_{10}H_6$, 1H), 7.79–7.90 (m, $-C_{10}H_6$, 3H), 8.33 (s, $-C_{10}H_6$, 1H), 9.80 (s, –NH, 1H).

4.2.3. *6-Decyloxynaphthalene-2-carboxylic acid hydrazide (**3c**)*

Yield: 82%. ^{1}H NMR (ppm, DMSO-d_6): 0.84 (t, $-CH_3$, 3H), 1.24–1.79 (m, $-CH_2$, 16H), 4.08 (t, $-OCH_2$, 2H), 4.51 (s, $-NH_2$, 2H), 7.18 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.34 (s, $-C_{10}H_6$, 1H), 7.83–7.90 (m, $-C_{10}H_6$, 3H), 8.33 (s, $-C_{10}H_6$, 1H), 9.82 (s, –NH, 1H).

4.2.4. *4-Methylbenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-CH_3)*

4-Methylbenzoyl chloride (0.5 g, 3.23 mmol) was added to a solution containing 0.93 g (3.23 mmol) of compound **3a** and 0.26 g (3.23 mmol) of pyridine in 10 ml of NMP. The reaction mixture was stirred for 12 h and then poured into water. The solid product was filtered and crystallized from methanol. Yield: 70%. ^{1}H NMR (ppm, DMSO-d_6): 0.83 (t, $-CH_3$, 3H), 1.21–1.80 (m, $-CH_2$, 8H), 2.38 (s, $-CH_3$, 3H), 4.10 (t, $-OCH_2$, 2H), 7.21 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.31 (d, $J=8.1$ Hz, $-C_6H_4$, 2H), 7.39 (s, $-C_{10}H_6$, 1H), 7.83–7.95 (m, $-C_{10}H_6$



Scheme. The synthetic route to 1,3,4-oxadiazole-based materials.

and –C_6H_4, 5H), 8.45 (s, –$C_{10}H_6$, 1H), 10.45 (s, –NH, 1H), 10.52 (s, –NH, 1H).

4.2.5. *4-Methylbenzoic acid N′-(6-octyloxynaphthalene-2-carbonyl)hydrazide (**4b**-CH₃)*

Yield: 69%. ^{1}H NMR (ppm, DMSO-d_6): 0.83 (t, –CH_3, 3H), 1.21–1.80 (m, –CH_2, 12H), 3.38 (s, –CH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.31 (d, J = 8.4 Hz, –C_6H_4, 2H), 7.39 (s, –$C_{10}H_6$, 1H), 7.83–7.96(m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.46 (s, –NH, 1H), 10.52 (s, –NH, 1H).

4.2.6. *4-Methylbenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-CH₃)*

Yield: 79%. ^{1}H NMR (ppm, DMSO-d_6): 0.84 (t, –CH_3, 3H), 1.24–1.78 (m, –CH_2, 16H), 2.38 (s, –CH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.31 (d, J = 7.8 Hz, –C_6H_4, 2H), 7.39 (s, –$C_{10}H_6$, 1H), 7.83–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.47 (s, –NH, 1H), 10.52 (s, –NH, 1H).

4.2.7. *4-Methoxybenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-OMe)*

Yield: 90%. ^{1}H NMR (ppm, DMSO-d_6): 0.88 (t, –CH_3, 3H), 1.21–1.81 (m, –CH_2, 8H), 3.87 (s, –OCH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.17 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.25 (d, J = 8.7 Hz, –$C_{10}H_6$, 1H), 7.42 (s, –$C_{10}H_6$, 1H), 7.79–8.11 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.63 (s, –$C_{10}H_6$, 1H), 10.39 (d, –NH, 2H).

4.2.8. *4-Methoxybenzoic acid N′-(6-octyloxynaphthalene-2-carbonyl)hydrazide (**4b**-OMe)*

Yield: 85%. ^{1}H NMR (ppm, DMSO-d_6): 0.86 (t, –CH_3, 3H), 1.22–1.81 (m, –CH_2, 12H), 3.83 (s, –OCH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.04 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.21 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H_6$, 1H), 7.90–7.96 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.39 (d, –NH, 2H).

4.2.9. *4-Methoxybenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-OMe)*

Yield: 82%. ^{1}H NMR (ppm, DMSO-d_6): 0.86 (t, –CH_3, 3H), 1.24–1.77 (m, –CH_2, 16H), 3.82 (s, –OCH_3, 3H), 4.10 (t, –OCH_2, 2H), 7.04 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.21 (d, J = 9.3 Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H_6$, 1H), 7.90–7.93 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.45 (s, –$C_{10}H_6$, 1H), 10.39 (d, –NH, 2H).

4.2.10. *4-Fluorobenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-F)*

Yield: 77%. ^{1}H NMR (ppm, DMSO-d_6): 0.88 (t, –CH_3, 3H), 1.23–1.81 (m, –CH_2, 8H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.34 (s, –$C_{10}H_6$, 1H), 7.37 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.87–8.03 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.58 (s, –NH, 2H).

4.2.11. *4-Fluorobenzoic acid N′-(6-octyloxynaphthalene-2-carbonyl)hydrazide (**4b**-F)*

Yield: 72%. ^{1}H NMR (ppm, DMSO-d_6): 0.85 (t, –CH_3, 3H), 1.26–1.80 (m, –CH_2, 12H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.34 (s, –$C_{10}H_6$, 1H), 7.37 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.88–8.04 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.58 (s, –NH, 2H).

4.2.12. *4-Fluorobenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-F)*

Yield: 72%. ^{1}H NMR (ppm, DMSO-d_6): 0.85 (t, –CH_3, 3H), 1.24–1.80 (m, –CH_2, 16H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.34 (s, –$C_{10}H_6$, 1H), 7.37 (d, J = 9 Hz, –C_6H_4, 2H), 7.87–8.04 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.55 (s, –NH, 2H).

4.2.13. *4-Chlorobenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-Cl)*

Yield: 80%. ^{1}H NMR (ppm, DMSO-d_6): 0.88 (t, –CH_3, 3H), 1.23–1.81 (m, –CH_2, 8H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H_6$, 1H), 7.60 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.88–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.60 (s, –NH, 1H), 10.64 (s, –NH, 1H).

4.2.14. *4-Chlorobenzoic acid N′-(6-octyloxynaphthalene-2-carbonyl)hydrazide (**4b**-Cl)*

Yield: 83%. ^{1}H NMR (ppm, DMSO-d_6): 0.86 (t, –CH_3, 3H), 1.26–1.81 (m, –CH_2, 12H), 4.11 (t, –OCH_2, 2H), 7.22 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H_6$, 1H), 7.60 (d, J = 8.7 Hz, –C_6H_4, 2H), 7.88–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.62 (s, –NH, 1H), 10.64 (s, –NH, 1H).

4.2.15. *4-Chlorobenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-Cl)*

Yield: 79%. ^{1}H NMR (ppm, DMSO-d_6): 0.84 (t, –CH_3, 3H), 1.24–1.80 (m, –CH_2, 16H), 4.11 (t, –OCH_2, 2H), 7.21 (d, J = 9 Hz, –$C_{10}H_6$, 1H), 7.38 (s, –$C_{10}H_6$, 1H), 7.60 (d, J = 8.4 Hz, –C_6H_4, 2H), 7.87–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 5H), 8.46 (s, –$C_{10}H_6$, 1H), 10.58 (s, –NH, 1H), 10.62 (s, –NH, 1H).

4.2.16. *4-Cyanobenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-CN)*

Yield: 77%. ^{1}H NMR (ppm, DMSO-d_6): 0.86 (t, –CH_3, 3H), 1.26–1.81 (m, –CH_2, 8H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 7.40 (s, –$C_{10}H$, 1H), 7.88–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 3H), 8.02–8.10 (m, –$C_{10}H_6$ and –C_6H_4, 4H), 8.46 (s, –$C_{10}H_6$, 1H), 10.67 (s, –NH, 1H), 10.82 (s, –NH, 1H).

4.2.17. *4-Cyanobenzoic acid N′-(6-octlyoxynaphthalene-2-carbonyl)hydrazide (**4b**-CN)*

Yield: 68%. ^{1}H NMR (ppm, DMSO-d_6): 0.84 (t, –CH_3, 3H), 1.26–1.81 (m, –CH_2, 12H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H$, 1H), 7.91–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 3H), 8.02–8.10 (m, –$C_{10}H_6$ and –C_6H_4, 4H), 8.46 (s, –$C_{10}H_6$, 1H), 10.67 (s, –NH, 1H), 10.82 (s, –NH, 1H).

4.2.18. *4-Cyanobenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-CN)*

Yield: 68%. ^{1}H NMR (ppm, DMSO-d_6): 0.82 (t, –CH_3, 3H), 1.24–1.80 (m, –CH_2, 16H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 7.39 (s, –$C_{10}H$, 1H), 7.88–7.97 (m, –$C_{10}H_6$ and –C_6H_4, 3H), 8.02–8.10 (m, –$C_{10}H_6$ and –C_6H_4, 4H), 8.46 (s, –$C_{10}H_6$, 1H), 10.68 (d, –NH, 2H).

4.2.19. *4-Nitrobenzoic acid N′-(6-hexyloxynaphthalene-2-carbonyl)hydrazide (**4a**-NO_2)*

Yield: 77%. ^{1}H NMR (ppm, DMSO-d_6): 0.88 (t, –CH_3, 3H), 1.22–1.81 (m, –CH_2, 8H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 7.41 (d, –$C_{10}H$, 1H), 7.88–7.97 (m, –$C_{10}H_6$, 3H), 8.15 (d, $J=9$ Hz, –C_6H_4, 2H), 8.39 (d, $J=9$ Hz, –C_6H_4, 2H), 8.47 (s, –$C_{10}H_6$, 1H), 10.70 (s, –NH, 1H), 10.90 (s, –NH, 1H).

4.2.20. *4-Nitrobenzoic acid N′-(6-octyloxynaphthalene-2-carbonyl)hydrazide (**4b**-NO_2)*

Yield: 83%. ^{1}H NMR (ppm, DMSO-d_6): 0.85 (t, –CH_3, 3H), 1.22–1.81 (m, –CH_2, 12H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=8.7$ Hz, –$C_{10}H_6$, 1H), 7.40 (d, –$C_{10}H$, 1H), 7.88–7.97 (m, –$C_{10}H_6$, 3H), 8.15 (d, $J=9$ Hz, –C_6H_4, 2H), 8.37 (d, $J=9$ Hz, –C_6H_4, 2H), 8.47 (s, –$C_{10}H_6$, 1H), 10.70 (s, –NH, 1H), 10.91 (s, –NH, 1H).

4.2.21. *4-Nitrobenzoic acid N′-(6-decyloxynaphthalene-2-carbonyl)hydrazide (**4c**-NO_2)*

Yield: 83%. ^{1}H NMR (ppm, DMSO-d_6): 0.84 (t, –CH_3, 3H), 1.24–1.81 (m, –CH_2, 16H), 4.11 (t, –OCH_2, 2H), 7.22 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 7.40 (d, –$C_{10}H$, 1H), 7.88–7.97 (m, –$C_{10}H_6$, 3H), 8.15 (d, $J=8.7$ Hz, –C_6H_4, 2H), 8.37 (d, $J=9.0$ Hz, –C_6H_4, 2H), 8.47 (s, –$C_{10}H_6$, 1H), 10.69 (s, –NH, 1H), 10.89 (s, –NH, 1H).

4.2.22. *2-(6-Hexyloxynaphthalen-2-yl)-5-p-tolyl-[1,3,4]oxadiazole (6-NPO-CH_3)*

Compound **4a**-CH_3 (0.8 g, 2.07 mmol) was dissolved in 10 ml of $POCl_3$; the mixture was heated at 130°C overnight, and then cooled to room temperature. Excess $POCl_3$ was removed at reduced pressure and the remaining mixture poured into water. The product was filtered and crystallized from methanol and chloroform to give a white solid; yield 42%. ^{1}H NMR (ppm, $CDCl_3$): 0.93 (t, –CH_3, 3H), 1.26–1.90 (m, –CH_2, 8H), 2.46 (s, –CH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.17 (s, –$C_{10}H_6$, 1H), 7.21 (d, $J=8.7$ Hz, –$C_{10}H_6$, 1H), 7.34 (d, $J=7.8$ Hz, –C_6H_4, 2H), 7.83(d, $J=8.4$ Hz, –$C_{10}H_6$, 2H), 7.85(d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 8.05 (d, $J=8.4$ Hz, –C_6H_4, 2H), 8.14 (d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 8.53 (s, –$C_{10}H_6$, 1H). Anal: calc. for $C_{25}H_{26}N_2O_2$ C 77.69, H 6.78, N 7.25; found C 77.98, H 6.80, N 6.85%. HRMS (EI) calc. 386.1994; found 386.1986.

4.2.23. *2-(6-Octyloxynaphthalen-2-yl)-5-p-tolyl-[1,3,4]oxadiazole (8-NPO-CH_3)*

White solid; yield 36%. ^{1}H NMR (ppm, $CDCl_3$): 0.93 (t, –CH_3, 3H), 1.26–1.90 (m, –CH_2, 12H), 2.46 (s, –CH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.17 (s, –$C_{10}H_6$, 1H), 7.21 (d, $J=8.7$ Hz, –$C_{10}H_6$, 1H), 7.34 (d, $J=7.8$ Hz, –C_6H_4, 2H), 7.83 (d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 7.85 (d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 8.06 (d, $J=8.4$ Hz, –C_6H_4, 2H), 8.14 (d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 8.53 (s, –$C_{10}H_6$, 1H). Anal: calc. for $C_{27}H_{30}N_2O_2$ C 78.23, H 7.29, N 6.76; found C 78.46, H 7.41, N 6.65%. HRMS (EI) calc. 414.2307; found 414.2312.

4.2.24. *2-(6-Decyloxy-naphthalen-2-yl)-5-p-tolyl-[1,3,4]oxadiazole (10-NPO-CH_3)*

White solid; yield 53%. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, –CH_3, 3H), 1.29–1.90 (m, –CH_2, 16H), 2.46 (s, –CH_3, 3H), 4.11 (t, –OCH_2, 2H), 7.17 (s, –$C_{10}H_6$, 1H), 7.21 (d, $J=9.3$ Hz, –$C_{10}H_6$, 1H), 7.34 (d, $J=8.4$ Hz, –C_6H_4, 2H), 7.82 (d, $J=8.7$ Hz, –$C_{10}H_6$, 1H), 7.85 (d, $J=8.4$ Hz, –$C_{10}H_6$, 1H), 8.06 (d, $J=8.4$ Hz, –C_6H_4, 2H), 8.14 (d, $J=9$ Hz, –$C_{10}H_6$, 1H), 8.53 (s, –$C_{10}H_6$, 1H). Anal: calc. for $C_{29}H_{34}N_2O_2$ C 78.70, H 7.74, N 6.33; found C 78.64, H 7.64, N 6.51%. HRMS (EI) calc. 442.2620; found 442.2617.

4.2.25. *2-(6-Hexyloxynaphthalen-2-yl)-5-(4-methoxy-phenyl)-[1,3,4]oxadiazole (6-NPO-OMe)*

White solid; yield 45%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, –CH_3, 3H), 1.30–1.90 (m, –CH_2, 8H), 3.91 (s, –OCH_3,

3H), 4.11 (t, $-OCH_2$, 2H), 7.04 (d, $J=9$ Hz, $-C_6H_4$, 2H), 7.17 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.82 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.10–8.17 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.52 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{25}H_{26}N_2O_3$ C 74.60, H 6.51, N 6.96; found C 74.27, H 6.55, N 6.80%. HRMS (EI) calc. 402.1943; found 402.1946.

4.2.26. *2-(6-Methoxyphenyl)-5-(6-octyloxynaphthalen-2-yl)-[1,3,4]oxadiazole (8-NPO-OMe)*

White solid; yield 51%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.30–1.90 (m, $-CH_2$, 12H), 3.91 (s, $-OCH_3$, 3H), 4.11 (t, $-OCH_2$, 2H), 7.03 (d, $J=9$ Hz, $-C_6H_4$, 2H), 7.16 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=8.7$ Hz, $-C_6H_4$, 2H), 7.82 (d, $J=8.1$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.1$ Hz, $-C_{10}H_6$, 1H), 8.10–8.17 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.51 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{27}H30N_2O_3$ C 75.32, H 7.02, N 6.51; found C 75.15, H 6.45, N 7.16%. HRMS (EI) calc. 430.2256; found 430.2248.

4.2.27. *2-(6-Decyloxynaphthalen-2-yl)-5-(4-methoxyphenyl)-[1,3,4]oxadiazole (10-NPO-OMe)*

White solid; yield 52%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (t, $-CH_3$, 3H), 1.28–1.90 (m, $-CH_2$, 16H), 3.91 (s, $-OCH_3$, 3H), 4.11 (t, $-OCH_2$, 2H), 7.04 (d, $J=9.3$ Hz, $-C_6H_4$, 2H), 7.16 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=9$ Hz, $-C_6H_4$, 2H), 7.82 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.11–8.17 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.52 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{29}H_{34}N_2O_3$ C 75.95, H 7.47, N 6.11; found C 76.10, H 7.22, N 5.89%. HRMS (EI) calc. 458.2569; found 458.2574.

4.2.28. *2-(4-Fluorophenyl)-5-(6-hexyloxynaphthalen-2-yl)-[1,3,4]oxadiazole (6-NPO-F)*

White solid; yield 87%. ^{1}H NMR (ppm, $CDCl_3$): 0.93 (t, $-CH_3$, 3H), 1.24–1.90 (m, $-CH_2$, 8H), 4.11 (t, $-OCH_2$, 2H), 7.18–7.28 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 7.83 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 8.13–8.22 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.53 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{24}H_{23}FN_2O_2$ C 73.83, H 5.94, N 7.17; found C 73.78, H 6.23, N 7.50%. HRMS (EI) calc. 390.1744; found 390.1740.

4.2.29. *2-(4-Fluorophenyl)-5-(6-octyloxynaphthalen-2-yl)-[1,3,4]oxadiazole (8-NPO-F)*

White solid; yield 81%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.31–1.90 (m, $-CH_2$, 12H), 4.11 (t, $-OCH_2$, 2H), 7.17–7.28 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 7.83 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.13–8.22 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.52 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{26}H_{27}FN_2O_2$ C 74.62, H 6.50, N 6.69%; found C 74.22, H 6.57, N 6.55%. HRMS (EI) calc. 418.2057; found 418.2055.

4.2.30. *2-(6-Decyloxy-naphthalen-2-yl)-5-(4-fluorophenyl)-[1,3,4]oxadiazole (10-NPO-F)*

White solid; yield 87%. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (t, $-CH_3$, 3H), 1.26–1.87 (m, $-CH_2$, 16H), 4.11 (t, $-OCH_2$, 2H), 7.17–7.28 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 7.84 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 8.14–8.23 (m, $-C_6H_4$ and $-C_{10}H_6$, 3H), 8.52 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{28}H_{31}FN_2O_2$ C 75.31, H 7.00, N 6.27; found C 75.58, H 7.18, N 6.09%. HRMS (EI) calc. 446.2370; found 446.2377.

4.2.31. *2-(4-Chloro-phenyl)-5-(6-hexyloxy-naphthalen-2-yl)-[1,3,4]oxadiazole (6-NPO-Cl)*

White solid; yield 68%. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (t, $-CH_3$, 3H), 1.25–1.90 (m, $-CH_2$, 8H), 4.07 (t, $-OCH_2$, 2H), 7.12 (s, $-C_{10}H_6$, 1H), 7.18 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.49 (d, $J=8.4$ Hz, $-C_6H_4$, 2H), 7.78 (d, $J=8.1$ Hz, $-C_{10}H_6$, 1H), 7.84 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.06–8.11 (m, $-C_{10}H_6$ and $-C_6H_4$, 3H), 8.46 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{24}H_{23}ClN_2O_2$ C 70.84, H 5.70, N 6.88; found C 70.97, H 5.74, N 6.77%. HRMS (EI) calc. 406.1448; found 406.1441.

4.2.32. *2-(4-Chlorophenyl)-5-(6-octyloxy-naphthalen-2-yl)-[1,3,4]oxadiazole (8-NPO-Cl)*

White solid; yield 72%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.33–1.91 (m, $-CH_2$, 12H), 4.09 (t, $-OCH_2$, 2H), 7.15 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.51 (d, $J=8.1$ Hz, $-C_6H_4$, 2H), 7.81 (d, $J=8.1$ Hz, $-C_{10}H_6$, 1H), 7.84 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.09–8.14 (m, $-C_{10}H_6$ and $-C_6H_4$, 3H), 8.50 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{26}H_{27}ClN_2O_2$ C 71.80, H 6.26, N 6.44; found C 71.46, H 6.33, N 6.29%. HRMS (EI) calc. 434.1761; found 434.1767.

4.2.33. *2-(4-Chlorophenyl)-5-(6-decyloxynaphthalen-2-yl)-[1,3,4]oxadiazole (10-NPO-Cl)*

White solid; yield 60%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (t, $-CH_3$, 3H), 1.25–1.89 (m, $-CH_2$, 16H), 4.10 (t, $-OCH_2$, 2H), 7.15 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.51 (d, $J=8.7$ Hz, $-C_6H_4$, 2H), 7.81 (d, $J=8.1$ Hz, $-C_{10}H_6$, 1H), 7.84 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.09–8.15 (m, $-C_{10}H_6$ and $-C_6H_4$, 3H), 8.51 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{28}H_{31}ClN_2O_2$ C 72.63, H 6.75, N 6.05; found C 72.76, H 6.87, N 5.90%. HRMS (EI) calc. 462.2074; found 462.2073.

4.2.34. *4-[5-(6-Hexyloxynaphthalen-2-yl)-[1,3,4]oxadiazol-2-yl]benzonitrile (6-NPO-CN)*

White solid; yield 52%. ^{1}H NMR (ppm, $CDCl_3$): 0.93 (t, $-CH_3$, 3H), 1.22–1.90 (m, $-CH_2$, 8H), 4.11 (t, $-OCH_2$, 2H), 7.18 (s, $-C_{10}H_6$, 1H), 7.23 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.84–7.88 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 8.13 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 8.29 (d, $J=9$ Hz, $-C_6H_4$, 2H), 8.54 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{25}H_{23}N_3O_2$ C 75.54, H 5.83, N 10.57; found C 75.29, H 6.05, N 10.55%. HRMS (EI) calc. 397.1790; found 397.1792.

4.2.35. *4-[5-(6-Octyloxynaphthalen-2-yl)-[1,3,4]oxadiazol-2-yl]benzonitrile (8-NPO-CN)*

White solid; yield 46%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.25–1.89 (m, $-CH_2$, 12H), 4.09 (t, $-OCH_2$, 2H), 7.15 (s, $-C_{10}H_6$, 1H), 7.21 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.81–7.86 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 8.12 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.25 (d, $J=8.1$ Hz, $-C_6H_4$, 2H), 8.50 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{27}H_{27}N_3O_2$ C 76.21, H 6.40, N 9.87; found C 76.21, H 6.46, N 9.70%. HRMS (EI) calc. 425.2103; found 425.2108.

4.2.36. *4-[5-(6-Decyloxynaphthalen-2-yl)-[1,3,4]oxadiazol-2-yl]benzonitrile (10-NPO-CN)*

Light yellow solid; yield 60%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (t, $-CH_3$, 3H), 1.28–1.90 (m, $-CH_2$, 16H), 4.11 (t, $-OCH_2$, 2H), 7.18 (s, $-C_{10}H_6$, 1H), 7.23 (d, $-C_{10}H_6$, 1H), 7.84–7.88 (m, $-C_{10}H_6$ and $-C_6H_4$, 4H), 8.13 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.28 (d, $J=8.7$ Hz, $-C_6H_4$, 2H), 8.54 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{29}H_{31}N_3O_2$ C 76.79, H 6.89, N 93.26; found C 76.70, H 7.03, N 9.29%. HRMS (EI) calc. 453.2416; found 453.2409.

4.2.37. *2-(6-Hexyloxynaphthalen-2-yl)-5-(4-nitrophenyl)-[1,3,4]oxadiazole (6-NPO-NO_2)*

Yellow solid; yield 70%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.25–1.90 (m, $-CH_2$, 8H), 4.11 (t, $-OCH_2$, 2H), 7.18 (s, $-C_{10}H_6$, 1H), 7.23 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.86 (d, $J=8.9$ Hz, $-C_{10}H_6$, 1H), 8.14 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.35–8.44 (m, $-C_6H_4$, 4H), 8.56 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{24}H_{23}N_3O_4$ C 69.05, H 5.55, N 10.07; found C 68.99, H 5.78, N 10.05. HRMS (EI) calc. 417.1689; found 417.1690.

4.2.38. *2-(4-Nitrophenyl)-5-(6-octyloxynaphthalen-2-yl)-[1,3,4]oxadiazole (8-NPO-NO_2)*

Yellow solid; yield 73%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 3H), 1.25–1.92 (m, $-CH_2$, 12H), 4.12 (t, $-OCH_2$, 2H), 7.18 (s, $-C_{10}H_6$, 1H), 7.24 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.4$ Hz, $-C_{10}H_6$, 1H), 7.87 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.14 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.36–8.45 (m, $-C_6H_4$, 4H), 8.57 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{26}H_{27}N_3O_4$ C 70.09, H 6.11, N 9.43; found C 70.38, H 6.20, N 9.05. HRMS (EI) calc. 445.2002; found 445.2004

4.2.39. *2-(6-Decyloxynaphthalen-2-yl)-5-(4-nitrophenyl)-[1,3,4]oxadiazole (10-NPO-NO_2)*

Yellow solid; yield 73%. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (t, $-CH_3$, 3H), 1.28–1.90 (m, $-CH_2$, 16H), 4.12 (t, $-OCH_2$, 2H), 7.19 (s, $-C_{10}H_6$, 1H), 7.24 (d, $-C_{10}H_6$, 1H), 7.85 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 7.87 (d, $J=9$ Hz, $-C_{10}H_6$, 1H), 8.15 (d, $J=8.7$ Hz, $-C_{10}H_6$, 1H), 8.36–8.45 (m, $-C_6H_4$, 4H), 8.57 (s, $-C_{10}H_6$, 1H). Anal: calc. for $C_{28}H_{31}N_3O_4$ C 71.01, H 6.60, N 8.87; found C 70.98, H 6.58, N 8.50. HRMS (EI) calc. 473.2315; found 473.2310.

References

[1] Lin, H. C., Lai, L. L., Hsieh, W. P., and Huang, W. Y., 1997, *Liq. Cryst.*, **22,** 661.

[2] Semmler, K. J. K., Dingemans, and Samulski, E. T., 1998, *Liq. Cryst.*, **258,** 85.

[3] Tokuhisa, H., Era, M., and Tsutsui, T., 1998, *Appl. Phys. Lett.*, **72,** 2639.

[4] Tokuhisa, H., Era, M., and Tsutsui, T., 1998, *Adv. Mater.*, **10,** 404.

[5] Sato, M., Ohta, R., Handa, M., and Kasuga, K., 2002, *Liq. Cryst.*, **29,** 1441.

[6] Karamysheva, L. A., Torgova, S. I., and Agafonova, I. F., 2000, *Liq. Cryst.*, **27,** 393.

[7] Cai, R., and Samulski, E. T., 1991, *Liq. Cryst.*, **9,** 617.

[8] Parra, M., Alderete, J., Zuniga, C., Hidalgo, P., Vergara, J., and Fuentes, G., 2002, *Liq. Cryst.*, **29,** 1375.

[9] Eichhorn, S. H., Paraskos, A. J., Kishikawa, E., and Swager, T. M., 2002, *J. Am. chem. Soc.*, **124,** 12742.

[10] Dimitrowa, K., Hauschild, J., Zaschke, H., and Schubert, H., 1980, *J. prakt. Chem.*, **331,** 631.

[11] Lai, C., Ke, Y. C., Su, J. C., Shen, C., and Li, W. R., 2002, *Liq. Cryst.*, **29,** 915.

[12] Kim, B. G., Kim, S., and Park, S. Y., 2001, *Tetrahedron Lett.*, **42,** 2697.

[13] Haristoy, D., and Tsiourvas, D., 2003, *Chem. Mater.*, **15,** 2079.

[14] Dingemans, T. J., Murthy, N. S., and Samulski, E. T., 2001, *J. phys. Chem. B.*, **105,** 8845.

[15] Fan, F. Y., Culligan, S. W., Mastrangelo, J. C., Katsis, D., and Chen, S. H., 2001, *Chem. Mater.*, **13,** 4584.

[16] Collings, P. J., and Hird, M., 1997, *Introduction to Liquid Crystals* (London: Taylor and Francis), p.71.

[17] Chandrasekhar, S., Nair, G. G., Rao, D. S. S., Praefcke, K., and Blunk, D., 1998, *Liq. Cryst.*, **24,** 67.

[18] Kishikawa, K., Harris, M. C., and Swager, T. M., 1999, *Chem. Mater.*, **11,** 867.

[19] Dingemans, T. J., and Samulski, E. T., 2000, *Liq. Cryst.*, **27,** 131.

[20] TAO, Y. T., BALASUBRAMANIAM, E., DANEL, A., JAROSZ, B., and TOMASIK, P., 2001, *Chem. Mater.*, **13,** 1207.
[21] WONG, M. S., LI, Z. H., TAO, Y., and D'IORO, M., 2003, *Chem. Mater.*, **15,** 1198.
[22] WAWAMOTO, M., MOCHIZUKI, H., SHISHIDO, A., TSUTSUMI, O., IKEDA, T., LEE, B., and SHIROTA, Y., 2003, *J. phys. Chem. B.*, **21,** 4887.
[23] GÜLLER, R., BINGGELI, A., BREU, V., BUR, D., FISCHLI, W., HIRTH, G., JENNY, C., KANSY, M., MONTAVON, F., MÜLLER, M., OEFNER, C., STADLER, H., VIEIRA, E., WILHELM, M., WOSTL, W., and MÄTKI, H. P., 1999, *Bioorg. med. Chem. Lett.*, **9,** 1403.
[24] DEBONO, M., TURNER, W. W., LAGRANDEUR, L., BURKHARDT, F. J., NISSEN, J. S., NICHOLS, K. K., RODRIGUEZ, M. J., ZWEIFEL, M. J., ZECKNER, D. J., GORDEE, R. S., TANG, J., and PARR, T. R., 1995, *J. med. Chem.*, **38,** 3271.