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The synthesis, characterization, and mesomorphic properties of a new type of heteronuclear compounds **1a–c** and a Pd complex **1d** derived from benzoxazole as the core group are reported. These compounds were prepared by the ring closure reaction of 4-alkoxybenzoic acid 4-[(4-alkoxy-2-hydroxyphenylimino)methyl]phenyl esters **6** in the presence of lead(IV) acetate. All the compounds were characterized by ^{1}H and ^{13}C NMR spectroscopies and elemental analysis. The phase behaviour of these mesogenic compounds was characterized and studied by differential scanning calorimetry and polarizing optical microscopy. All the compounds **1a** exhibited nematic (N) and/or smectic C (SmC) phases, as expected for rod-like molecules; however, the compounds **1b** and **1c** exhibited crystal phases. For those compounds **1a** having shorter carbon chains (n=1, 3, 4) nematic phases were observed, whereas for compounds having longer carbon chains (n=6, 7, 8, 10, 12, 14) smectic C behaviour was also observed at lower temperatures. The greater aspect ratio (l/d) of compounds **1a** compared with **1b** and **1c** was found to be required for the observation of liquid crystallinity. The fluorescent properties of these compounds were also examined. All λ_{max} peaks of the absorption and photoluminescence spectra of compounds **1a–1c** occurred at *c.* 316–322 nm and 371–382 nm, respectively. The quantum yields of some compounds were relatively low, and also slightly solvent-dependent.

1. Introduction

Interest in the study of mesomorphic heterocyclic compounds has dramatically increased in recent years due to their wider range of structural templates, as well as their optical and photochemical properties. The introduction of heterocyclic rings into core structures to generate mesogenic materials has been well demonstrated [1, 2]. Numerous unique structures with a variety of molecular shapes have been synthesized and found to exhibit interesting mesomorphic properties. The phases observed included traditional columnar [2] and calamitic mesophases. These heterocyclic structures generally incorporated unsaturated atoms, such as O, N, S and/or others, and the presence of such electronegative atoms often resulted in a reduced symmetry for the overall molecules; and a stronger polar induction. The use of these unique heterocyclic structures to produce materials of low symmetry or/and non-planar structures may be technologically important for device applications. On the other hand, the polar induction by N, O, and/or S atoms on these heterocyclic cores may be responsible

for the formation and enhancement of mesophases in this class of compound.

Numerous compounds exhibiting interesting mesophases have been prepared and studied, among these, 5- or 6-membered rings have been used due to the range of structures and/or known chemistry. The enhancement of mesomorphic properties [2, 3] in this type of heterocyclic structure was believed to be due to their unsaturation and/or greater polarizability. In addition, a lower symmetry and/or non-planar structure caused by the N, O, S or other atoms incorporated in such heterocyclic rings may probably lead to the mesomorphic properties observed. These types of heterocyclic compounds, if designed appropriately, offer an opportunity to produce metal-containing mesogenic materials (metallomesogens).

Benzoxazole derivatives, an important class of heterocyclic compounds, have been studied in a variety of research areas over recent years. Most of the studies have been focused on, bioactivity [4, 5], non-linear optics (NLO) [6], organic light-emitting diodes (OLED) [7], and polymeric materials [8]. By comparison, examples of liquid crystals based on benzoxazole as mesogenic core are relatively limited [9]. Nematic benzothiazol **1e** was first reported by Vorländer and

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Weisswange in 1925 [10]. More recent work by Zúñiga *et al.* was reported on similar compounds based on benzothiazol units containing amides and azo as linking groups [11]. Nematic and/or smectic C mesophases formed by these rod-like compounds were observed. In addition, a number of benzothiazole-derived compounds were found to exhibit interesting photophysical and fluorescent properties by Iwata *et al.* [12] and Gallas *et al.* [13]. As part of our continuing studies of heterocyclic mesogens [3], in this paper we describe the synthesis, characterization and mesomorphic properties of a series of calamitic benzoxazole derivatives; their fluorescent properties were also examined.
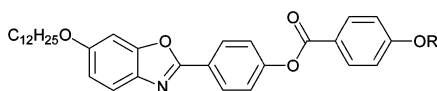
1a   R = (CH₂)ₙH; n = 1, 3, 4, 6, 7, 8 10, 12, 14
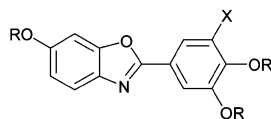
R = (CH₂)ₙH
1b   X = H; n = 12
1c   X = OR; n = 14
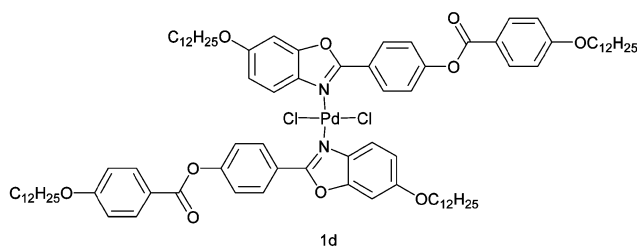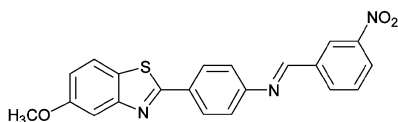

1d

1e

2. Results and discussion

2.1. *Synthesis and characterization*

A variety of synthetic methods [14–16] for benzoxazole derivatives have been reported; these compounds are typically prepared by condensation of 2-aminophenols with benzaldehydes or benzoic acid and subsequent intramolecular cyclization. The synthetic procedures used in this work for the benzoxazole derivatives **1a–1c**

are summarized in schemes 1 and 2. The preparation of benzoxazole derivatives involved first the nitration of 3-alkoxyphenols by concentrated nitric acid and sodium nitrite at 0°C to give 2-nitro-5-dodecyloxyphenols **3** in low yields of 30–46%. The reaction of 2-amino-5-dodecyloxyphenol, (which was obtained by hydrazine reduction of 2-nitro-5-dodecyloxyphenol **3**) and substituted benzaldehydes **5** in refluxing absolute ethanol led to the esters **6**. The final benzoxazoles **1a** and **1b** were obtained by reaction of substituted esters **6** or phenols **7** with Pb(OAc)₄ in refluxing chloroform. The yields were relatively high in the range 85–92%. ¹H and ¹³C NMR spectroscopies were used to characterize the intermediates and the final products. For example, a singlet peak appeared at δ 8.62 ppm and is characteristically observed for imine-H (–CH=N–) group of compounds **6**; this peak disappeared upon formation of final products **1a–1c**.

2.2. *Mesomorphic properties*

The liquid crystalline behaviour of compounds **1a–1c** was characterized and studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The phase transitions and thermodynamic data are summarized in table 1. All compounds **1a** formed liquid crystalline phases regardless of the alkoxy chain length, but the type of mesophase was dependent on the chain length. The compounds **1a** with shorter chains (*n*=1, 3, 4) exhibited nematic phases, while, the compounds with longer chains (*n*=6, 7, 8, 10, 12, 14) exhibited nematic and smectic C phases. The fact that the derivative **1a** with methoxy (*n*=1) as the terminal chain was a nematic indicated that the terminal 4′-dodecyloxy chain on the benzoxazole ring was essential for the formation of mesophases. Elongation of the overall molecule by increasing the length of the terminal chain led to the formation of the more ordered smectic C phases. This may probably be attributed to an enhanced dispersive interaction between the terminal chains.

The temperature ranges of the nematic phases shown by compounds **1a** (*n*=1, 3, 4) were 47.6–59.6°C on heating. The nematic phase was observed and identified on the basis of optical textures, as shown in figure 1. The clearing temperatures of the compounds ranged from 152.8°C (*n*=1) to 139.3°C (*n*=14), and decreased slightly as the chain length increased. The enthalpies of the nematic–isotropic, transition were in the range 0.41 kJ mol⁻¹ (*n*=1)−2.00 kJ mol⁻¹ (*n*=14), and increased with increasing chain length. This slight increase in enthalpies indicated that the phase became more ordered as the chain length increased. In contrast, for compounds **1a** with longer chain lengths (*n*=6, 7, 8,
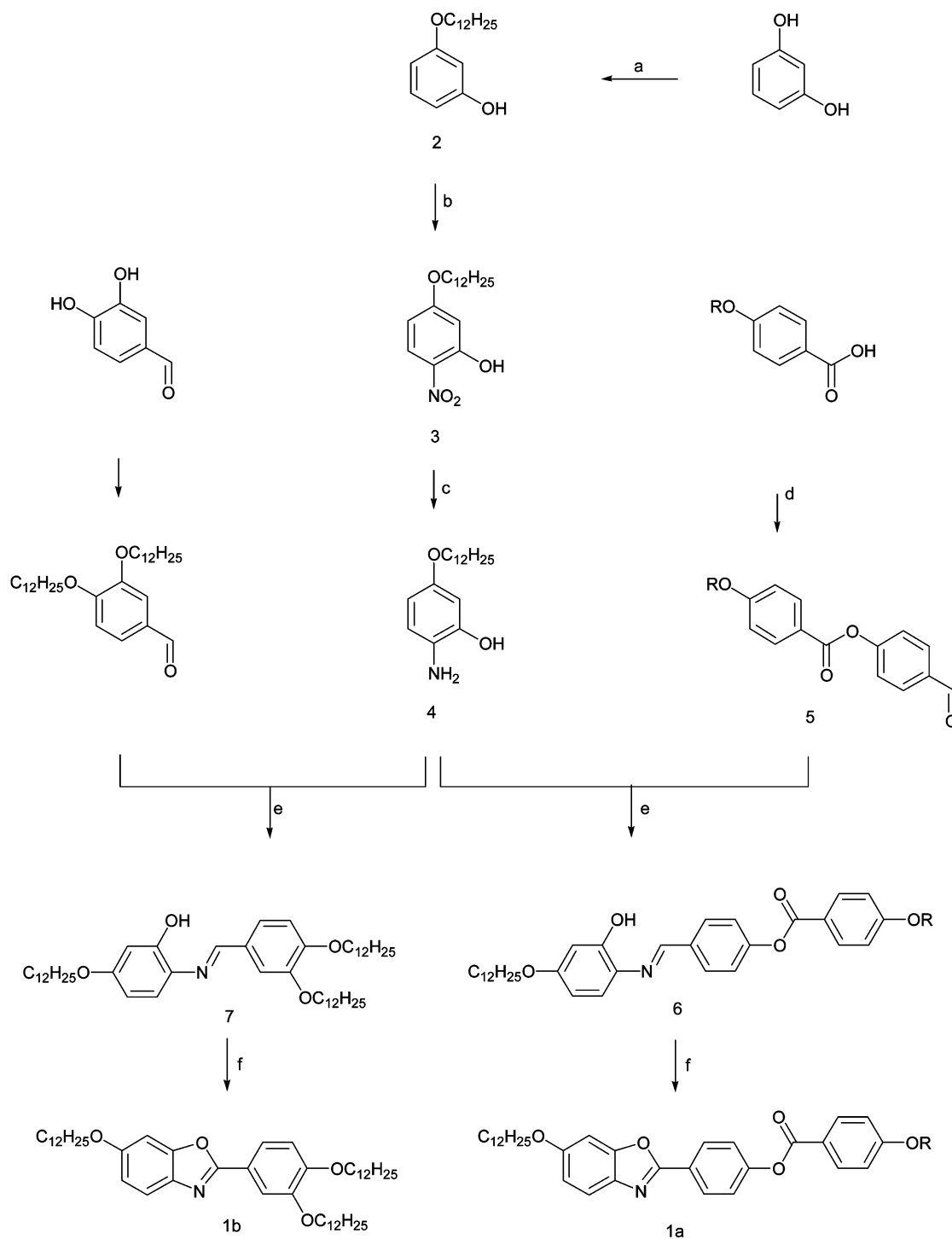
Scheme 1. Reagents and conditions. a: KHCO₃ (1.1 eq), RBr (1.1 eq), KI (cat.), refluxed in CH₃COCH₃, 48 h, 70–85%; b: NaNO₂ (0.5 eq), HNO₃ (1.1 eq), stirred at 0°C, in CH₂Cl₂, 6 h, 30–40%; c: N₂H₄ (1.1 eq), Pd/C (1.1 eq), refluxed in EtOH, 4 h, 80–88%. d: DCC (1.2 eq), DMAP (1.2 eq), stirred in THF at rt, 24 h, 48–58%; e: CH₃COOH (drops), refluxed in EtOH, 24 h, 85–95%; f: Pb(OAc)₄ (1.1 eq), refluxed in CHCl₃, 2 h, 80–85%.

10, 12, 14) two transitions, Cr–SmC and N–I were observed in the DSC analyses. Monotropic phase behaviour was observed for compound **1a**, *n*=6. The characteristic schlieren texture was used to identify the smectic C phases (see figure 1) and were observed on cooling the nematic phases of the compounds. The
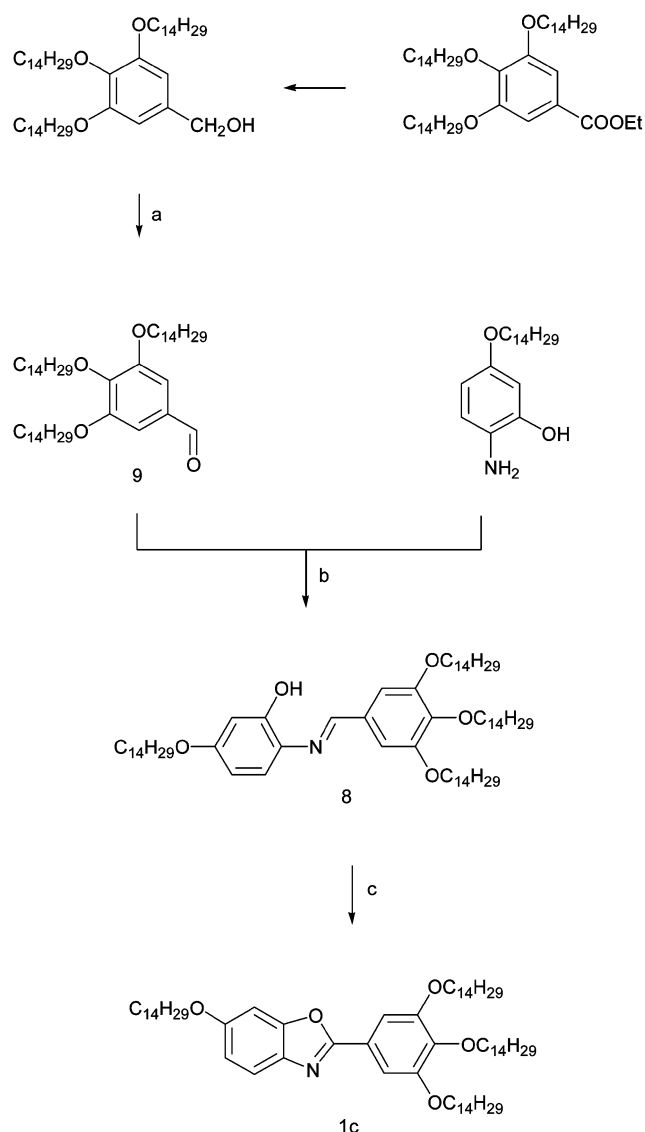
Scheme 2. Reagents and conditions. a: pyridinium chloro-chromate (2.0 eq), stirred at rt in CH_2Cl_2, 3 h., 75–85%. b: CH_3COOH (drops), refluxed in EtOH, 24 h, 79–85%; c: $Pb(OAc)_4$ (1.1 eq), refluxed in $CHCl_3$, 2 h, 77–82.

temperatures of the smectic–nematic transition were quite sensitive to the chain length, and increased from 99.8°C ($n=7$) to 136.6°C ($n=14$) on heating. The enthalpies of the smectic–nematic transition also increased with chain length, i.e. $\Delta H=0.01\,kJ\,mol^{-1}$ ($n=7$) to $1.38\,kJ\,mol^{-1}$ ($n=14$). This increase in transition enthalpies was in fact parallel to the increase in the nematic–isotropic enthalpy found for compounds with shorter chain lengths ($n=1, 3, 4$). The results indicated that the temperature range of the nematic phase was decreased (i.e. 48.3→2.70°C) but the temperature range of the smectic C phase was increased (i.e. 11.1→56.4°C) as the chain length increased. Nevertheless, the overall

temperature range of the mesophases was relatively insensitive to the chain length, i.e. 47.6–59.6°C.

In order to understand the relationship between the molecular shape and the observed phases, the compounds **1b,1c** were also prepared. In compounds **1b,1c** several alkoxy chains were directly attached to the terminal phenyl ring of the benzoxazole core; similar compounds, but with a smaller length/width ratio (i.e. aspect ratio), were obtained. However, these two compounds formed only crystal phases, and melting points of 90.4 and 65.6°C were observed for compound **1b** and **1c**, respectively. Increasing the length of the terminal alkoxy chains, which altered the overall molecular shape from rod-like to more lath-like, only led to a dramatic lowering of melting points.

The X-ray diffraction (XRD) patterns for some of the compounds **1a** ($n=10, 12, 14$) were measured at 100°C, in the smectic C phase. Figure 2 shows a representative XRD pattern of **1a** ($n=12$). The layer spacing was measured as 40.48 Å, whereas the molecular length from MM2 calculations is 44.66 Å. The layer spacing deviates slightly from the calculated value, and tilt angles from the director of 24.6° ($n=10$), 27.8° ($n=12$) and ~29.6° ($n=14$) were approximately estimated. In addition, the layer spacing of the compounds correlated well with chain lengths (39.00 Å for $n=10$ and 42.19 Å for $n=14$).

One palladium complex **1d** ($n=12$) was prepared from benzoxazole **1a**, to understand the influence of the metal atom on mesogenic behaviour in such a complex. However, the palladium complex was found to be non-mesogenic, and a melting temperature at 194.6°C was observed. This melting temperature was higher than that of the uncoordinated mesogenic benzoxazole (**1a**, $n=12$) by c. 52.6°C. The loss of mesomorphic behaviour in this Pd complex may probably be attributed to a combination of the increased rigidity and non-planar structure of the complex. The geometry at the palladium(II) centre is normally square planar, and two *trans*-chlorine atoms are believed to be perpendicular to the molecular plane determined by two benzoxazole rings as shown in figure 3.

2.3. Optical properties

Benzoxazole derivatives have been studied with regard to their photophysical [17–20] and fluorescent properties. The luminescent properties observed for such heterocyclic compounds are greatly affected by substituents and/or conjugation lengths at the 2-position of the rings [21]. Some benzoxazole derivatives have been used as emitters in EL devices [22–23]. The UV-Vis absorption spectra of compounds **1a–1c** in CH_2Cl_2 solution are presented in figure 4. The absorption and emission spectra of all compounds **1a–1c** were very

Table 1. Phase transition temperatures and associated enthalpies of compounds **1a–1c**. n represents the number of carbons in the alkoxy chain. Cr=crystal phase; SmC=smectic C phase; N=nematic phase; I=isotropic. Transition temperatures ($^\circ$C) and enthalpies (in parenthesis, kJ mol^{-1} determined by DSC at a scan rate of 10.0°C min^{-1}.

Compound		Cr		SmC		N		I
1a; $n = 1$			Cr		104.5 (69.3) / 82.1 (67.5) →	N	152.8 (0.41) / 152.5 (0.38) →	I
3			Cr		95.1 (34.5) / 75.1 (36.6) →	N	142.7 (0.54) / 141.8 (0.51) →	I
4			Cr		95.6 (29.4) / 71.5 (30.1) →	N	148.5 (0.51) / 148.2 (0.70) →	I
6	Cr	66.9 (47.3) →	SmC	86.8 (28.1) / 78.1 (0.14) →	N	146.4 (0.82) / 145.1 (0.87) →	I
7	Cr	88.7 (67.5) / 64.9 (24.9) →	SmC	99.8 (0.10) / 99.4 (0.12) →	N	143.4 (0.80) / 142.6 (0.80) →	I
8	Cr	87.6 (61.4) / 65.3 (50.6) →	SmC	118.0 (0.02) / 117.1 (0.03) →	N	145.4 (0.84) / 145.1 (0.90) →	I
10	Cr	88.5 (69.2) / 62.1 (57.4) →	SmC	128.7 (0.26) / 128.2 (0.25) →	N	143.4 (1.36) / 142.4 (1.53) →	I
12	Cr	91.2 (65.4) / 61.7 (61.5) →	SmC	134.7 (0.72) / 134.3 (0.68) →	N	142.0 (2.00) / 141.4 (2.05) →	I
14	Cr	80.2 (53.3) / 62.6 (51.2) →	SmC	136.6 (1.38) / 135.5 (1.36) →	N	139.3 (2.06) / 138.4 (2.03) →	I
1b; $n = 12$						Cr	90.4 (67.6) / 65.0 (67.3) →	I
1c; $n = 14$						Cr	65.6 (135.0) / 34.6 (111.0) →	I
1d						Cr	194.6 (30.8) / 174.7 (16.2) →	I

similar in shape because of their structural similarity. However, a small shoulder at *c.* 340 nm was observed for compounds **1b** and **1c**. The highest absorption peaks of all the compounds were found to be insensitive to chain length and/or numbers of terminal chains, and all occurred at *c.* 316–320 nm for **1a** and 320–322 nm for **1b–1c**. The data associated with λ_{max} peaks are listed in table 2. Increasing the numbers of electron-donating groups (**1a**→**1b**, **1c**) produces a slight red shift, and also a clear broad shoulder at *c.* 340–342 nm.

The photoluminescence (PL) spectra measured in CH$_2$Cl$_2$ of compounds **1a–1c** are shown in figure 5. A similar trend to that seen in absorption was observed in the photoluminescence spectra. The emission peaks occurred at 373.4–382.4 nm for **1a** and 371.2–373.4 nm for **1b,1c**. The solution PL spectra of **1b,1c**, though slightly more complex, were quite similar in peak shape to those of the UV-Vis spectra; these results suggest that the geometric correlation in the ground states is retained in the excited states. However, the quantum yields of some compounds in CH$_2$Cl$_2$ estimated with anthracene

as a standard (φ_f=0.27 in hexane) were relatively low [24]. For example, the yield was 2.34% and −3.22% for compounds **1a** and **1b**, respectively. The quantum yields were slightly dependent on the solvents used and emission wavelength (e.g. increased by *c.* 1.2% in THF for **1a**; n=12).

3. Experimental

3.1. *Characterization*

All chemicals and solvents were reagent grades from Lancaster Co. or Aldrich Chemical Co; solvents were dried by standard techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 instrument. FTIR spectra were obtained on a Nicolet Magna-IR 550 spectrometer. DSC thermographs were run on a Mettler DSC 821 and calibrated with a pure indium sample (m.p.=156.60°C, 28.45 J K); all phase transitions were determined using a scan rate of 10.0° min^{-1}. Optical polarizing microscopy was carried out with a Zeiss AxiaPlan instrument equipped with a Mettler FP90/
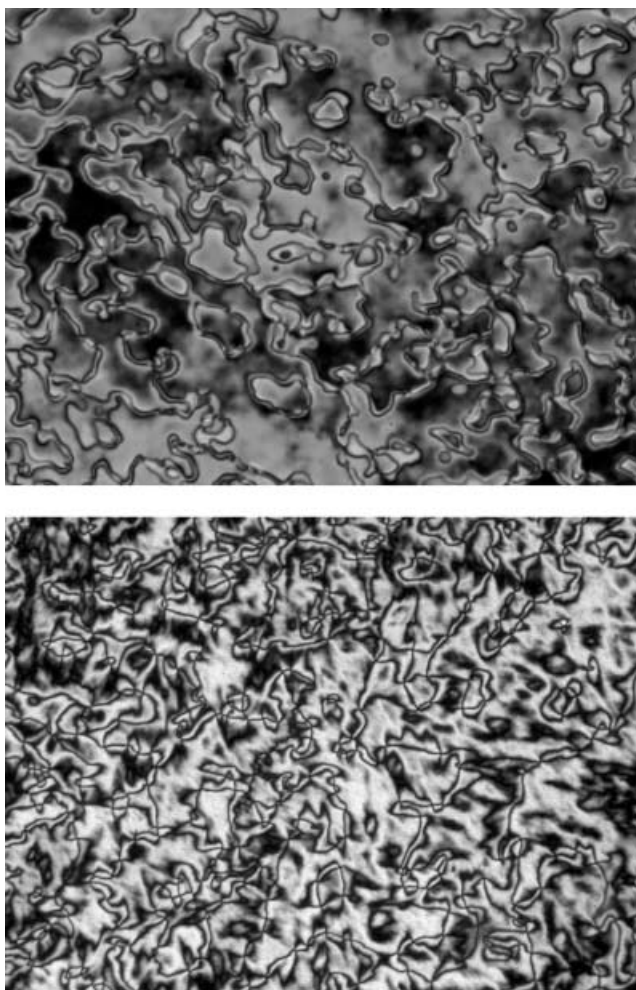
Figure 1. Optical textures (100×) of nematic phase (top) at 135°C and SmC phase (bottom) at 110°C observed for compound **1a** (*n*=8).

FP82HT hot stage system. UV-Vis absorption and fluorescence spectra were obtained using a Hitachi F-4500 or Jasco V-530 spectrometer. The UV-Vis absorption and PL spectra of all compounds were measured in degassed CH_2Cl_2 solution at room temperature. The PL spectra were obtained with λ_{max} values of the UV-Vis spectra as excitation wavelengths; for example, 320 nm for **1a**, 325 nm for **1b** and **1c**. Elemental analysis for C, H and N were conducted on a Heraeus Vario EL-III elemental analyser at National Taiwan University; data were listed in table 3. The 4-alkoxybenzoic acids, 3,4-ditetradecyloxybenzaldehyde and 3,4,5-tritetradecyloxy-benzaldehyde **9** were prepared by literature procedures [3].

3.2. *Synthesis*

3.2.1. 3-Dodecyloxyphenol (2). (20.0 g, 0.18 mol), $KHCO_3$ (27.03 g, 0.27 mol), 1-bromotetradecane (55.4 g,
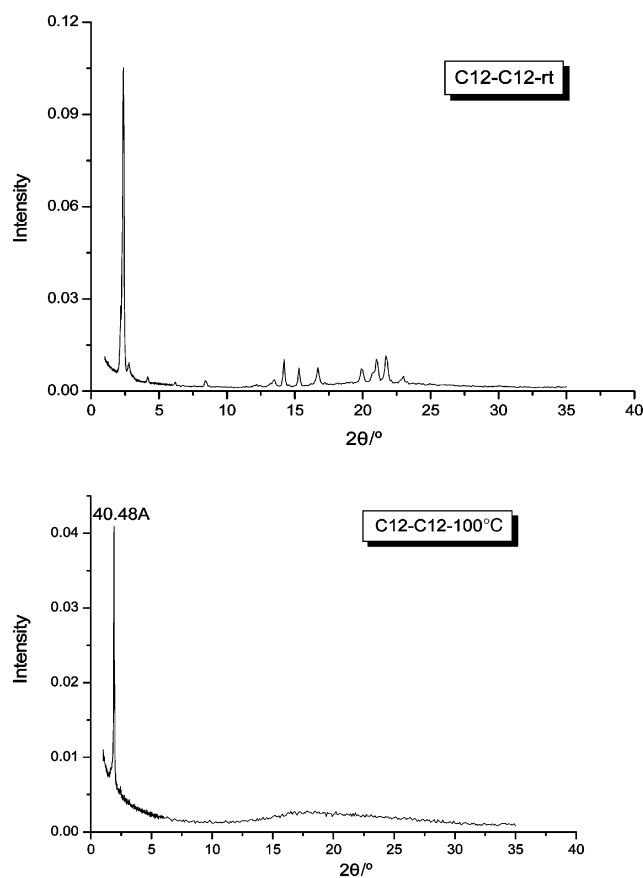
Figure 2. Powder XRD pattern of compound **1a** (*n*=12) measured at r.t. (top) and 100°C (bottom).
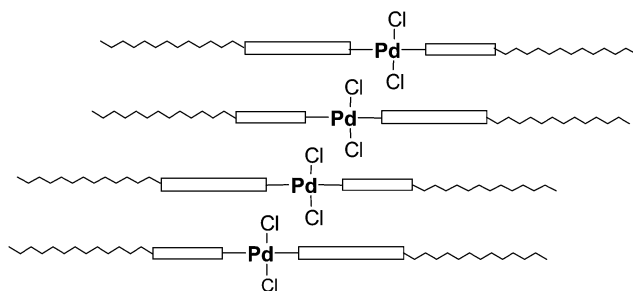
Figure 3. Schematic representation of possible arrangement (side view) in Pd complexes.

0.20 mol) and KI (1.50 g) were dissolved in 350 ml of dry acetone under nitrogen. The solution was heated under reflux for 24 h, then concentrated and extracted with 200 ml dichloromethane/water (1/3). The organic layers were collected and dried over anhydrous $MgSO_4$. The product was purified by flash chromatography (silica gel) with hexane/ethyl acetate (15/1). A white solid was obtained after recrystallization from hexane; yield 62%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H,

Figure 4. Normalized absorption spectra of compounds **1a**–**1c** in (CH₂Cl₂) solution.

Table 2. Photophysical properties of compounds **1a**–**1c**: spectra measured in CH_2Cl_2 solution.

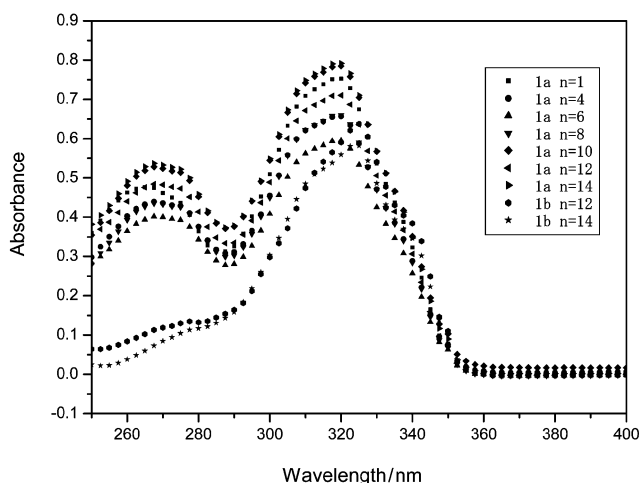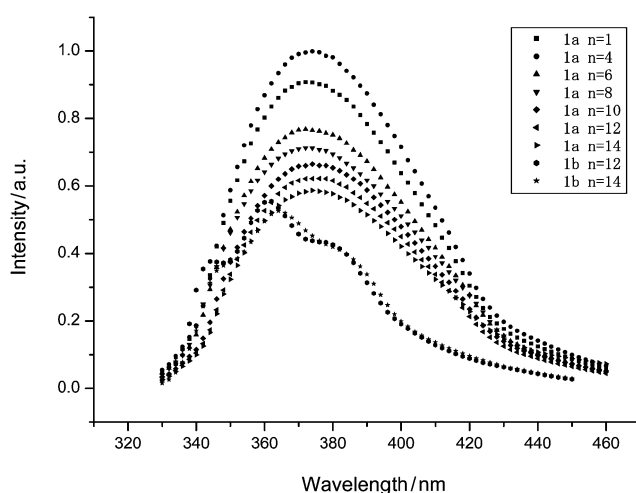| Compound	λ_{max} abs/nm	λ_{max} EM/nm
1a; $n=1$	320	373.4
3	319	377.4
4	316	379.8
6	316	378.0
8	320	381.8
10	319	377.6
12	320	380.2
14	320	382.4
1b; $n=12$	322	371.2
1c; $n=14$	320	373.4

Figure 5. Normalized PL spectra of compounds **1a**–**1c** in CH_2Cl_2 solution.

Table 3. Elemental analysis data (%) for compounds **1** with calculated values in parentheses.

Compound	C	H	N
1a; $n=1$	74.61 (74.83)	7.47 (7.42)	2.63 (2.62)
3	75.26 (75.37)	7.88 (7.77)	2.49 (2.51)
4	75.36 (75.63)	7.96 (7.93)	2.42 (2.45)
6	75.68 (76.09)	8.24 (8.23)	2.31 (2.34)
7	76.11 (76.31)	8.34 (8.37)	2.25 (2.28)
8	76.52 (76.30)	8.51 (8.55)	2.23 (2.07)
10	76.91 (76.41)	8.76 (8.94)	2.14 (2.18)
12	77.13 (77.27)	9.27 (8.99)	1.87 (2.05)
14	77.60 (77.58)	9.20 (9.33)	1.97 (1.80)
1b; $n=12$	78.84 (78.66)	11.04 (10.91)	1.66 (1.87)
1c; $n=14$	79.63 (79.33)	11.78 (11.67)	1.15 (1.34)

–CH₃, $J=6.65$ Hz), 1.17–1.45 (m, 18H, –CH₂), 1.67–1.81 (m, 2H, –CH₂), 3.90 (t, 2H, –OCH₂, $J=6.62$ Hz), 5.02 (br, 1H. Ar–OH), 6.36–6.49 (m, 3H, Ar–H), 7.10 (t, 1H, Ar–H, $J=8.41$ Hz). ¹³C NMR (CDCl₃): δ 14.09, 22.66, 29.20, 29.37, 29.58, 29.61, 29.64, 31.90, 68.06, 102.05, 107.03, 107.58, 130.04, 156.69, 160.47. IR (neat): 3452 (–OH) cm⁻¹.

3.2.2. 5-Dodecyloxy-2-nitrophenol (3). A mixture of 3-dodecyloxyphenol (9.19 g, 33.0 mmol) and NaNO₂ (0.45 g, 6.6 mmol) dissolved in 150 ml of CH₂Cl₂ was added dropwise to concentrated nitric acid (1.76 ml, 39.0 mmol) in an ice bath. The solution was stirred for 6 h at room temperature, then concentrated and extracted twice with 100 ml dichloromethane/water (1/1). The organic layers were collected and dried over anhydrous MgSO₄. The product was purified by flash chromatography (silica gel) with hexane/ethyl acetate (40/1). The product was isolated as yellow solids after recrystallization from hexane/CH₂Cl₂; yield 34%. ¹H NMR (CDCl₃): δ 0.86 (t, 3H, –CH₃, $J=6.74$ Hz), 1.24–1.38 (m, 18H, –CH₂), 1.74–1.82 (m, 2H, –OCH₂), 3.99 (t, 2H, –OCH₂, $J=6.40$ Hz), 6.45–6.51 (m, 2H, Ar–H), 8.00 (d, 1H, Ar–H, $J=10.02$ Hz), 11.03 (s, 1H, Ar–OH). ¹³C NMR (CDCl₃): δ 14.10, 22.66, 28.81, 29.25, 29.26, 29.32, 29.49, 29.54, 29.6, 31.90, 69.12, 101.76, 109.82, 126.89, 127.51, 157.98, 166.72. IR (neat): 3184 (–OH) cm⁻¹.

3.2.3. 2-Amino-5-dodecyloxyphenol (4). Powdered palladium on activated carbon (0.076 g, 10% Pd) was added to a solution of compound **3** (2.50 g, 7.73 mmol) dissolved in absolute ethanol, and the mixture was heated gently at reflux for 0.5 h. Hydrazine monohydrate (2.00 ml, 42.0 mmol) in 10.0 ml of absolute ethanol was added dropwise to the solution. The mixture was returned to reflux for a further 4 h. The solution was filtered to remove solids, then

concentrated to give a light yellow solid. An off-white solid was obtained after recrystallization from ethanol; yield 88%. ^{1}H NMR (CDCl$_3$): δ 0.86(t, 3H, –CH$_3$, $J=6.74$ Hz), 1.24–1.38 (m, 18H, –CH$_2$), 1.67–1.71 (m, 2H, –CH$_2$), 3.84 (t, 2H, –OCH$_2$, $J=6.50$ Hz), 6.42–6.29 (m, 2H, Ar–H), 6.74(d, 1H, Ar–H, $J=7.6$ Hz), 11.03 (s, 1H, Ar–OH). ^{13}C NMR (CDCl$_3$): δ 14.11, 23.1, 28.81, 29.25, 29.26, 29.32, 29.49, 29.54, 29.6, 31.90, 72.3, 102.23, 107.61, 117.18, 125.55, 144.50, 162.23. IR (neat): 3352, 3268 (–NH$_2$) cm^{-1}.

3.2.4. 4-(4′-Decyloxybenzoyloxy)benzaldehyde (5).

To a solution of 4-decyloxybenzoic acid (10.0 g, 0.034 mol), dimethylaminopyridine (DMAP; 5.01 g, 0.041 mol) and *N,N′*-dicyclohexylcarbodiimide (*DCC*; 8.46 g, 0.041 mol) in dry THF (100 ml) under nitrogen, was added 4-hydroxybenzaldehyde (5.72 g, 0.04 mol), and the solution stirred at room temperature for 30 h. The solution was concentrated to dryness and the solids extracted with CH$_2$Cl$_2$/H$_2$O (1/1). The organic layers were collected, dried over MgSO$_4$, and then concentrated to afford a grey solid. The product was purified by column chromatography (SiO$_2$, hexane/ethylacetate 20/1). To give a white solid; yield 47%. ^{1}H NMR (CDCl$_3$): δ 0.84–0.87 (m, 3H, –CH$_3$), 1.22–1.33 (m, 14H, –CH$_2$), 1.76–1.80 (m, 2H, –CH$_2$), 4.02 (t, 2H, –OCH$_2$, $J=6.54$ Hz), 6.95 (d, 2H, Ar–H, $J=5.24$ Hz), 7.36 (d, 2H, Ar–H, $J=8.43$ Hz), 7.92 (d, 2H, Ar–H, $J=8.46$ Hz), 8.10 (d, 2H, Ar–H, $J=8.78$ Hz), 9.98 (s, 1H, Ar–COH). ^{13}C NMR (CDCl$_3$): δ 14.05, 22.62, 25.92, 29.30, 30.85, 31.53, 31.84, 68.35, 114.39, 120.75, 122.55, 131.16, 162.38, 133.85, 155.88, 163.84, 164.18, 190.93.

3.2.5. 4-Decyloxybenzoic acid 4-[(4-dodecyloxy-2-hydroxyphenylimino)methyl]phenyl ester (6).

A hot solution of compound **4** (2.46 g, 8.4 mmol) in 100 ml of absolute ethanol was slowly added to a solution of compound **5** (3.0 g, 7.8 mmol) in 50 ml of absolute ethanol. Acetic acid (0.50 ml) was added to the mixture, which was heated gently at reflux for 24 h. Yellow solids were filtered and collected. The product was obtained after recrystallization from CH$_2$Cl$_2$/hexane; yield 95%. ^{1}H NMR (CDCl$_3$): δ 0.83–0.87 (m, 6H, –CH$_3$), 1.25 (m, 32H, –CH$_2$), 1.77–1.80 (m, 4H, –CH$_2$), 3.92 (t, 2H, –OCH$_2$, $J=6.6$ Hz), 4.03 (t, 2H, –OCH$_2$, $J=6.5$ Hz), 6.46 (d, 1H, Ar–H), 6.56 (d, 1H, Ar–H), 6.96 (d, 2H, Ar–H, $J=8.89$ Hz), 7.24–7.34 (m, 3H, Ar–H), 7.96 (d, 2H, Ar–H, $J=8.43$ Hz), 8.13 (d, 2H, Ar–H, $J=8.89$ Hz), 8.62(s, 1H, Ar–CH=N–Ar). ^{13}C NMR (CDCl$_3$): δ 13.97, 22.53, 25.87, 29.21, 31.77, 68.12, 100.33, 106.98, 114.21, 116.03, 121.01, 122.15, 128.13, 129.37, 132.20, 133.62, 152.25, 153.09, 153.64, 160.17, 163.56, 164.46.

3.2.6. 5-Dodecyloxy-2-[(3,4-didodecyloxybenzylidene)amino]phenol (7).

This was prepared by a process similar to that used for compound **6** (see scheme 1); yield 85%. ^{1}H NMR (CDCl$_3$): δ 0.84–0.87 (m, 9H, –CH$_3$), 1.24–1.49 (m, 54H, –CH$_2$), 3.93 (t, 2H, –OCH$_2$, $J=6.59$ Hz), 4.03 (t, 2H, –OCH$_2$, $J=5.27$ Hz), 4.06 (t, 2H, –OCH$_2$, $J=5.28$ Hz), 6.43 (dd, 1H, Ar–H, $J=2.68$, 4.35 Hz), 6.55 (d, 1H, Ar–H, $J=2.65$ Hz), 6.89 (d, 1H, $J=4.14$ Hz), 7.20 (d, 1H, Ar–H, $J=8.88$ Hz), 7.28 (dd, 1H, Ar–H, $J=1.66$, 8.26 Hz), 7.49(s, 1H, Ar–H), 8.49(s, 1H, Ar–COH). ^{13}C NMR (CDCl$_3$): δ 14.12, 22.68, 26.00, 26.03, 29.13, 29.23, 29.24, 29.34, 29.36, 29.39, 29.44, 29.57, 29.62, 29.65, 29.69, 29.70, 68.92, 68.26, 69.11, 69.30, 100.49, 106.93, 111.31, 112.55, 116.12, 123.71, 128.93, 129.29, 149.42, 152.16, 153.31, 153.86, 159.75.

3.2.7. 5-Tetradecyloxy-2-[(3,4,5-tritetradecyloxybenzylidene)-amino]phenol (8).

This was prepared by a process similar to that used for compound **6** (see scheme 2); yield 80%. ^{1}H NMR (CDCl$_3$): δ 0.85–0.87 (m, 12H, –CH$_3$), 1.23–1.47 (m, 88H, –CH$_2$), 1.78–1.84 (m, 8H, –CH$_2$), 3.93 (t, 2H, –OCH$_2$ $J=6.59$ Hz), 4.00 (m, 6H, –OCH$_2$), 6.44 (dd, 1H, Ar–H, $J=2.69$, 8.80 Hz), 6.55 (d, 1H, Ar–H, $J=2.68$ Hz), 7.05 (d, 2H, Ar–H, $J=5.09$ Hz), 7.20(d, 1H, Ar–H, $J=8.94$ Hz), 8.46(s, 1H, Ar–H). ^{13}C NMR (CDCl$_3$): δ 14.11, 22.69, 26.03, 26.11, 29.22, 29.37, 29.38, 29.42, 29.60, 29.65, 29.67, 29.69, 29.71, 29.75, 30.35, 31.93, 68.28, 69.26, 73.60, 100.51, 106.80, 107.02, 116.22, 128.73, 131.24, 141.21, 153.44, 153.93, 160.02.

3.2.8. 6-Dodecyloxy-2-(3,4-didodecyloxyphenyl)benzoxazole (1b).

This is a general procedure for compounds **1a**, **1b** and **1c**. (see schemes 1 and 2). Compound **7** (3.00 g, 4.00 mmol) was dissolved in 150 ml of hot CHCl$_3$ and the solution slowly mixed with lead acetate (2.43 g, 10.8 mmol). The mixture was heated gently at reflux for 2 h; the solution was then filtered off, and concentrated to give a light brown solid. This was redissolved in CH$_2$Cl$_2$ and extracted twice with water; the organic layers were collected and dried over anhydrous MgSO$_4$. The product was purified by flash chromatography with hexane/CH$_2$Cl$_2$ (2/1), and a white solid was isolated after recrystallization from CH$_2$Cl$_2$/CH$_3$OH; yield 85%. ^{1}H NMR (CDCl$_3$): δ 0.84–0.87 (m, 9H, –CH$_3$), 1.24–1.49 (m, 54H, –CH$_2$), 1.78–1.86 (m, 6H, –CH$_2$), 3.98 (t, 2H, –OCH$_2$, $J=6.56$ Hz), 4.05 (t, 2H, –OCH$_2$, $J=6.60$ Hz), 4.10 (t, 2H, –OCH$_2$, $J=6.55$ Hz), 6.91–6.95 (m, 2H, Ar–H), 7.06 (s, 1H, Ar–H), 7.60 (d, 1H, Ar–H, $J=8.68$ Hz), 7.74–7.77 (m, 2H, Ar–H, $J=6.05$ Hz). ^{13}C NMR (CDCl$_3$): δ 14.12, 22.70, 26.00, 26.05, 29.13, 29.23, 29.36, 29.38, 29.40, 29.44, 29.59, 29.65, 29.67, 29.71, 31.94, 68.93, 69.16, 69.40, 96.18, 111.96, 112.88, 113.37, 119.13, 121.02, 149.29, 151.29, 152.26, 157.70,

162.45. Anal: calcd for $C_{49}H_{81}NO_4$, C 78.66, H 10.91, N 1.87; found, C 78.84, H 11.04, N 1.66%.

3.2.9. 4-Decyloxybenzoic acid 4-(6-dodecyloxyben-zoxazol-2-yl)phenyl ester (1a).

Yield 80%. ^{1}H NMR (CDCl$_3$): δ 0.88–0.84 (m, 6H, –CH$_3$), 1.25–1.46 (m, 32H, –CH$_2$), 1.78–1.83 (m, 4H, –CH$_2$), 3.99 (t, 2H, –OCH$_2$, $J=6.51$ Hz), 4.03 (t, 2H, –OCH$_2$, $J=6.53$ Hz), 6.92–6.97 (m, 3H, Ar–H), 7.08 (s, 1H, Ar–H), 7.35 (d, 2H, Ar–H, $J=8.63$ Hz), 7.60 (d, 1H, Ar–H, $J=8.72$ Hz), 8.13 (d, 2H, Ar–H, $J=8.74$ Hz), 8.24 (d, 2H, Ar–H, $J=8.61$ Hz). ^{13}C NMR (CDCl$_3$): δ 14.09, 22.66, 26.00, 29.34, 31.90, 68.36, 68.88, 96.07, 113.42, 114.38, 119.90, 121.12, 122.39, 124.90, 128.48, 132.35, 135.73, 151.69, 153.29, 157.85, 161.54, 163.74, 164.53. Anal: calcd for $C_{42}H_{57}NO_5$, C 76.91, H 8.76, N 2.14; found C 76.41, H 8.94, N 2.18%.

3.2.10. 6-Tetradecyloxy-2-(3,4,5-tritetradecyloxyphenyl) benzoxazole (1c).

Yield 85%. ^{1}H NMR (CDCl$_3$): δ 0.84–0.87 (m, 12H, –CH$_3$), 1.23–1.47 (m, 88H, –CH$_2$), 1.78–1.84 (m, 8H, –CH$_2$), 3.97–4.09 (m, 8H, –OCH$_2$), 6.94 (d, 1H, Ar–H, $J=6.53$ Hz), 7.07 (s, 1H, Ar–H), 7.44 (s, 2H, Ar–H), 7.63 (d, 1H, Ar–H, $J=8.71$ Hz). ^{13}C NMR (CDCl$_3$): δ 14.12, 22.70, 26.06,2 6.08, 26.11, 29.21, 29.38, 29.39, 29.42, 29.59, 29.60, 29.66, 29.68, 29.69, 29.72, 29.76, 30.36, 31.94, 68.95, 69.37, 73.63, 96.17, 105.88, 113.67, 119.25, 120.89, 141.49, 151.30, 153.51, 157.95, 162.34. Anal: calcd for $C_{69}H_{121}NO_5$, C 79.33, H 11.67, N 1.34; found, C 79.63, H 11.78, N 1.15%.

3.2.11. Dichloro palladium(II) complex of 4-alkoxybenzoic acid 4-(6-dodecyloxy benzoxazol-2-yl)-3-hydroxyphenyl ester (1d).

4-Octyloxybenzoic acid 4-(6-dodecyloxybenzoxazol-2-yl)-3-hydroxyphenyl ester (0.30 g, 0.446 mmol) dissolved in 30 ml of hot absoute ethanol/THF (10/1), and the solution was slowly added to a solution of palladium(II) chloride (0.05 g, 0.28 mmol) in 10 ml absoute ethanol. The mixture was heated under reflux for 20 h, then cooled to room temperature and the yellow solids filtered off. The product was isolated as a yellow solid after recrystallization from THF/ethanol; yield 80%. Anal: calcd for $C_{88}H_{122}Cl_2N_2O_{10}Pd$, C 68.40, H 7.96, N 1.81; found C 68.85, H 8.03, N 1.78%.

4. Conclusions

A series of heterocyclic mesogenic compounds based on benzoxazole as the core group was prepared; these compounds exhibited nematic and smectic C phases. The presence of nitrogen/ and oxygen atoms, which are more polarizable in the heterocyclic ring, is believed to be responsible for the formation of mesomorphic properties. The larger aspect ratio—length/width (l/d)—of compounds **1a** compared with **1b**, **1c** is used to account for the formation of the observed mesophases. A structural modification in this type of heterocyclic derivative is needed to enhance the quantum yields of these compounds for materials applications.

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