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The effect of polar substituents on the heterocyclic benzoxazoles

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Abstract—The synthesis, characterization, and mesomorphic properties of a new type of heterocyclic compounds **1**, **2** derived from benzoxazole are reported. In order to understand the relationship between the structure and the mesomorphic behavior, compounds containing a variety of polar substituents (i.e., X=H, F, Cl, Br, CH_3, CF_3, OCH_3, NO_2, CN, OH, NMe_2, $COOCH_3$) on the terminal end were prepared. The phase behavior of these mesogenic compounds was characterized and studied by differential scanning calorimetry (DSC) and polarization optical microscopy. The formation of mesophases was strongly dependent on the electronic and/or the steric factors of the substituents. In general, a mesophase was better induced by introduction of a polar substituent. Compounds (X=H) formed a crystalline phase, however, other compounds, except for X=OH, exhibited nematic or smectic A phases. Interestingly all compounds with electron-donating substituents (X=CH_3, OCH_3, NMe_2) exhibited nematic phases, however, other compounds with electron-withdrawing substituents (X=F, Cl, Br, CF_3, NO_2, CN, $COOCH_3$) formed smectic A phases. Compounds (X=NO_2, CN, $COOCH_3$) have higher clearing temperatures than those of other homologues, and the higher T_{cl} was attributed to an enhanced conjugative interaction. However, no linear correlation between the clearing temperature or the temperature range of mesophases with Hammett σ_p constants was found. The fluorescent properties of the compounds were examined. All λ_{max} peaks of the absorption and photoluminescence spectra of compounds occurred at ca. 348–381 and 389–478 nm, respectively. Whereas, the quantum yields of some compounds were relatively low.

1. Introduction

A delicate balance of molecular interactions in a specific state[1] is crucially essential to the formation of a predesigned structure. This is particularly important in liquid crystalline materials, and liquid crystals form a state of matter intermediate between the solid and the liquid. This type of molecular interaction[1c,d] induced to form mesophases can be weak dipole–dipole interaction, dispersion, H-bonding, coordinative force, and others. Forces which are too strong or too weak can lead to the formation of a solid or liquid state.

Numerous heterocyclic compounds[2] derived from compounds such as 1,3,4-oxadiazole,[3] 1,2,4-triazole,[4] and benzoxazole[5] exhibiting interesting mesophases have recently been explored due to their varieties in structures and/or known chemistry. Better mesomorphic behavior[6] formed by these heterocyclic structures was attributed to their unsaturation and/or more polarizable nature. On the other hand, a lower symmetry[3] and/or non-planar structure caused by nitrogen, oxygen, sulfur, or other atoms incorporated on such heterocyclic rings also explained the preferred or better mesomorphic properties. Materials with lower melting temperatures, potential candidates for further applications, are often generated by such compounds. It is well known that the stability[7] of the mesophase may be augmented by an increase of the polarity or polarization along the mesogenic core of the molecule. A substantial change of the micro- as well as macro-polarizability in a specific structure or molecule can be easily achieved by the introduction of polar substituent along the preferred molecular direction. The effect of polar substituents in a variety of mesogenic systems[8] has been studied and investigated during the past years. Some predictions were successfully made in terms of mesomorphic behavior. The transition temperature of M→I has been correlated with the polarizability anisotropy of bonds to the substituent in 4-(4-substituted phenylazo)-phenyl-4-alkoxybenzoates.[8d] Previous studies[7,8c] also showed that compounds substituted with polar groups, such as –NO_2, –CN, might lead to a higher clearing temperature, which has been attributed to the conjugative interaction increase between the substituent and the ester moiety. On the other hand, the effect of polar substituents on the mesogenic 1,3,4-oxadiazoles-based materials was also studied. The mesophase and optical properties of these oxadiazole materials[3a] were also found to be strongly influenced by the presence of a terminal polar group.

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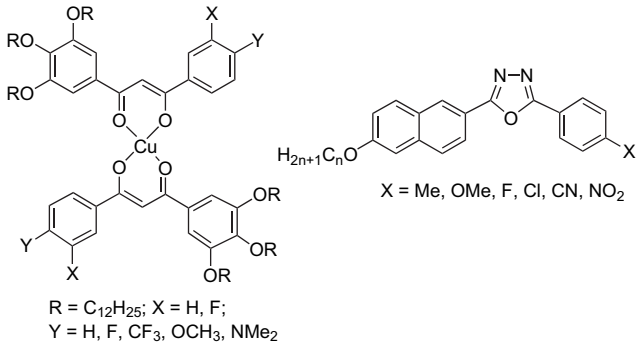
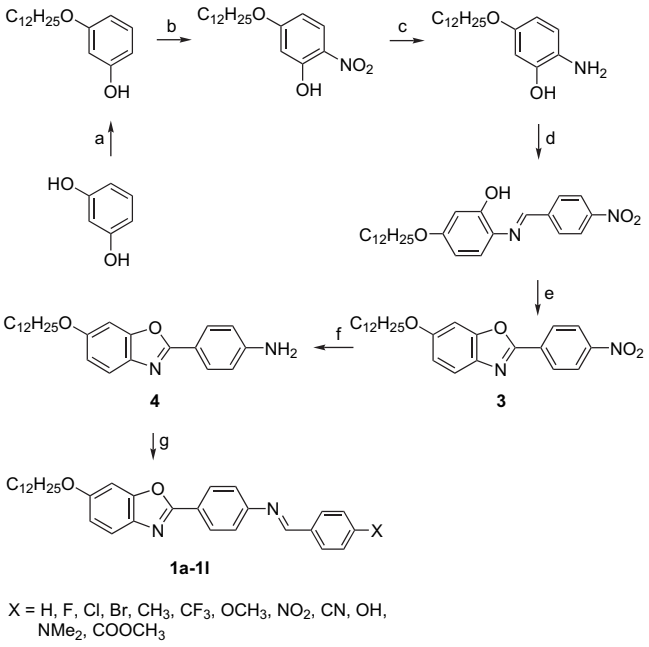


Benzoxazoles, as an important type of heterocyclic compound, have been studied in a variety of research areas, including non-linear optics (NLO),[9] organic light-emitting diodes (OLED),[10] and polymeric materials.[11] However, benzoxazole derivatives exhibiting mesophases[5a,12] have been less often reported. Nematic or/and smectic C mesophases formed by these rod-like compounds were observed. Benzothiazole-derived compounds were also found to have photophysical and fluorescent applications.[13] In a previous paper, the substituent effect on the columnar formation in β-diketonate metallomesogens[14] was investigated. A rectangular columnar phase (Col_r) was observed for substituents with bulkier groups (i.e., X=Me, Et), however, a hexagonal columnar phase (Col_h) was observed for substituents with electron-withdrawing groups (i.e., X=Cl, Br, I). Interestingly, a satisfactory linear relationship with a correlation coefficient of 0.974 between the clearing temperatures and Hammett σ_p constants was obtained for the copper complexes.

As part of our studies of heterocyclic mesogens, in this paper, we describe the synthesis, characterization, and the mesomorphic properties of a series of calamitic benzoxazole derivatives with various substituents on the terminal phenyl ring. Their fluorescent properties were also examined. Nematic or smectic phases were observed depending on the electronic nature of the substituents. However, the observed optical properties were not sensitive to the substituents except for the compound with an NMe_2 group.

2. Results and discussion

The synthetic procedures[5a] for the benzoxazole derivatives **1a**–**1l** are summarized in Scheme 1. The majority of benzoxazole-based derivatives were prepared by the condensation of 2-aminophenols with benzaldehydes or benzoic acid and subsequent intramolecular cyclization. The compounds of 5-dodecyloxy-2-nitrophenol, 2-amino-5-dodecyloxyphenol, 5-dodecyloxy-2-[(4-nitrobenzylidene)amino]phenol, 6-dodecyloxy-2-(4-nitrophenyl)benzoxazole **3**, and 4-(6-dodecyloxybenzoxazol-2-yl)phenylamine **4** were prepared by reported procedures.[5a] The final compounds, benzylidene-4-(6-dodecyloxybenzoxazol-2-yl)phenylamine were prepared by the condensation reaction of 4-(6-dodecyloxybenzoxazol-2-yl)phenylamine and appropriate aldehydes in refluxing absolute ethanol with a yield ranging from 67–82%. ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis were used to characterize the intermediates and the final products.



Scheme 1. Reactions and reagents: (a) RBr (1.1 equiv), $KHCO_3$ (1.3 equiv), KI, refluxed in dry CH_3COCH_3, 48 h, 60 °C; (b) HNO_3 (1.2 equiv), $NaNO_2$ (0.2 equiv), stirred at 0 °C in CH_2Cl_2, 12 h, 25 °C; (c) N_2H_4 (1.2 equiv), Pd/C (0.1 equiv), refluxed in absolute C_2H_5OH, 6 h, 85 °C; (d) 4-Nitrobenzaldehyde (1.0 equiv), CH_3COOH (drops), refluxed in absolute C_2H_5OH, 12 h, 90 °C; (e) $Pb(OAc)_4$ (1.3 equiv), refluxed in CH_2Cl_2, 6 h, 85 °C; (f) N_2H_4 (1.2 equiv), Pd/C (0.1 equiv), refluxed in absolute ethanol, 6 h, 80%; (g) substituted benzaldehyde (1.0 equiv), CH_3COOH (drops), refluxed in absolute C_2H_5OH, 12 h, 68–90 °C.

2.1. Mesomorphic properties

The mesomorphic behavior of compounds **1a**–**1l** was characterized and studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. The phase transitions and thermodynamic data were summarized in Table 1. In order to study the substituent effect on the formation of the mesophases, a variety of compounds with a variety of polar groups (i.e., X=H, F, Cl, Br, CH_3, CF_3, OCH_3, NO_2, CN, OH, NMe_2, $COOCH_3$) substituted on the opposite end of the benzoxazole ring were studied. Among these polar groups, some are known as strong π-acceptors (i.e., X=CN, NO_2) or π-donors (X=Cl, Br, OH), and others are known as intermediate (X=Cl, $COOCH_3$), besides being classified as electron-donating or electron-withdrawing groups. The results indicated that the formation of mesophases in this type of electron-deficient heterocyclic system was strongly dependent on the electronic and/or the steric factors of the substituents. Compound **1a** (X=H) was in fact non-mesogenic. A transition of crystal-to-isotropic at 99.8 °C was observed, and the lack of liquid crystallinity of compound **1a** can probably be attributed to the insufficient dipole over the entire molecule. When a polar functional group was substituted on the phenyl ring located on the opposite side to the benzoxale core, the mesomorphic properties were improved. All compounds except for **1j** (X=OH) were truly mesogenic, in which introducing a polar group was used to enhance or/and induce the formation of the mesophases. The results also indicated that compounds (**1e**, **1g**, **1k**) with an electron-donating substituent (–CH_3, OCH_3, NMe_2) exhibited nematic (N) phases, however, other

Table 1. Phase transitions and enthalpies of compounds **1a**–**1l**

1a					Cr	99.8 (60.1) / 79.8 (60.8)	I	
1b			Cr	101.7 (59.2) / 74.9 (56.7)	SmA	155.6 (4.25) / 154.7 (4.12)	I	
1c	Cr_1	82.4 (2.03)	Cr_2	92.1 (45.3) / 74.3 (10.3)	SmA	174.0 (4.24) / 173.2 (3.28)	I	
1d	Cr_1	63.3 (14.6) / 50.0 (25.5)	Cr_2	97.9 (59.9) / 80.2 (13.1)	SmA	194.3 (6.42) / 192.8 (6.36)	I	
1e			Cr	103.9 (55.4) / 86.7 (56.5)	N	137.4 (0.38) / 137.0 (0.40)	I	
1f			Cr	90.8 (47.6) / 75.3 (50.4)	SmA	180.9 (6.22) / 179.5 (6.11)	I	
1g	Cr_1	92.0 (4.61)	Cr_2	108.3 (51.6) / 76.3 (51.5)	N	169.5 (0.49) / 169.2 (0.47)	I	
1h	Cr_1	95.6 (2.28) / 88.1 (1.96)	Cr_2	129.3 (7.85) / 127.0 (8.03)	SmA	224.8 (2.64) / 224.2 (2.66)	I	
1i	Cr_1	102.9 (8.93) / 86.3 (6.08)	Cr_2	120.7 (40.1) / 102.7 (30.7)	SmA	219.1 (3.27) / 217.3 (3.21)	I	
1j					Cr	130.7 (16.7) / 117.2 (16.4)	I	
1k	Cr_1	123.3 (34.6) / 111.8 (33.8)	SmX	156.7 (0.29) / 156.2 (0.23)	N	161.0 (0.60) / 160.5 (0.53)	I	
1l	Cr_1	103.1 (35.6)	Cr_2	133.0 (51.6) / 115.2 (12.7)	SmA	212.5 (5.68) / 210.8 (5.54)	I	

Cr_1, Cr_2=crystalline phases, SmX=unidentified smectic phase, SmC=smectic C phase, SmA=Smectic A phase, N=nematic phase, I=isotropic phase.

compounds (**1b**, **1c**, **1d**, **1f**, **1h**, **1i**, **1l**) with an electron-withdrawing substituent (–F, –Cl, –Br, $–CF_3$, $–NO_2$, –CN, $–COOCH_3$) formed smectic A (SmA) phases. The N and SmA phases were observed and identified by optical texture, as shown in Figure 1.

Among them, compounds **1b**, **1c** , **1d** formed SmA phases, however, compound **1d** containing a larger and/or more polarized group (X=Br) enhanced the SmA phase more than compounds with a smaller and/or less polarized group (X=F, Cl). The clearing temperature of compound **1d** was higher than those of compounds **1b** and **1c**, i.e., 194.3 °C>174.0 °C>155.6 °C. This order in clearing temperatures and the temperature of mesophase was parallel to the increased polarizability in the order of Br>Cl>F. On the other hand, the temperature range of the mesophase was also wider for compound **1d** than those of compounds **1a** and **1b**, i.e., 96.4 °C>81.9 °C>53.9 °C on heating. Interestingly, among these electron-withdrawing substituents, compounds **1h**, **1i**, **1l** (X=NO_2, CN, $COOCH_3$) appeared to have clearing temperatures higher than those of other homologues, which ranged from 212.5 and 224.8 °C. These polar groups are also known as good π-acceptors, and have a more planar structure (i.e., sp or sp^2 hybrid orbital). The increase in T_{cl} might be attributed to two factors. Electronically, a conjugative interaction over the entire molecule was better achieved between the polar substituent and the other side of benzoxazole, and also a better packing arrangement due to a more overall molecular planar structure may be achieved in the solid and liquid crystal states. The temperature range of mesophases were relatively wide with these three compounds, at ca. 79.5 °C (**1l**)–98.4 °C (**1i**). Among these three substituents, the NO_2 group is particularly worthy to note. Compound **1h** (X=NO_2) has the highest clearing temperature in the whole series, and this is probably due to NO_2 group having the largest dipole. The range of mesophase temperature is relatively high; 98.4 °C (**1i**; CN)>96.4 °C (**1d**; Br)>95.5 °C (**1h**; NO_2). The effect of lateral and terminal $–NO_2$ as a substituent in achiral calamitic liquid crystals has been reviewed.[8e] The results indicated that substantial changes in clearing and/or melting temperatures were obviously observed depending on the molecular structures and the substituted position. A polar NO_2 group attached to the hydrocarbon moiety changes substantially the electron affinity of the molecules, and the strong mesomeric effect caused by the NO_2 group induces a positive charge on the nitrogen atom and increases the electronegativity of the group.[8e,15] The transition enthalpies of SmA→I in the whole series of the compounds, measured with 2.64 kJ/mol (**1h**)–6.42 kJ/mol (**1d**), varied slightly with the substituents. On the other hand, compounds **1e** and **1f**, which are relatively equal in molecular size, exhibited a different mesophase; N phase for **1e** and SmA phase for **1f**, respectively. On the other hand, a higher T_{cl} in compound **1f** (180.9 °C) over **1e** (137.4 °C) by ca. 43.4 °C, as well as a wider mesophase range by ΔT=56.6 °C

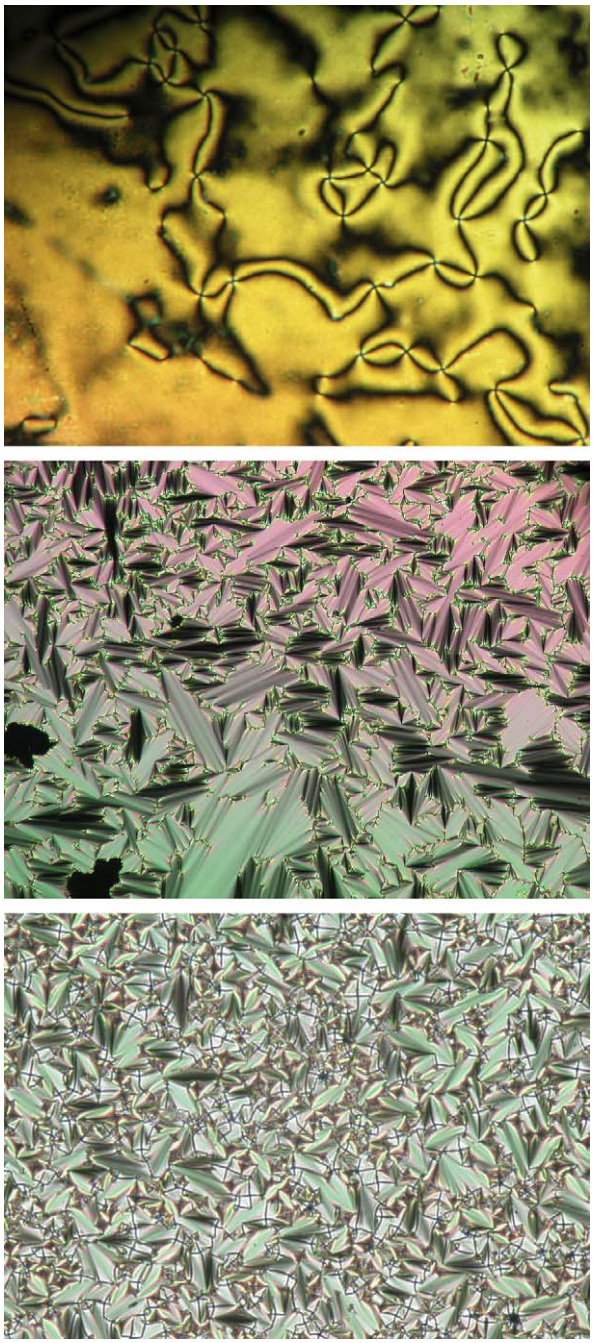


Figure 1. Optical textures observed by **1e** (X=CH_3) at 119.0 °C (top plate), **1f** (X=CF_3) at 165.0 °C (middle plate), and **1l** (X=$COOCH_3$) at 175.0 °C (bottom plate).

(i.e., 90.1 °C for **1f** vs 33.5 °C for **1e**) might be attributed to a better or larger dipole on **1f** (CF_3) over **1e** (CH_3). The electronic factor of the substituent, but not the steric factor, might have played a more important role in forming or inducing the phase. Heterocyclic benzoxazole is known as an electron-deficient moiety, and polarization or electron distribution by an electron-donating group, such as –CH_3, is better achieved by compound **1f** than by compound **1e**. Compound **1g** formed a N phase.

The transition enthalpies of N→I, measured with 0.38 kJ/mol (**1e**)–0.60 kJ/mol (**1k**), were insensitive to the substituents. Compound **1j** (X=OH) was non-mesogenic, and only

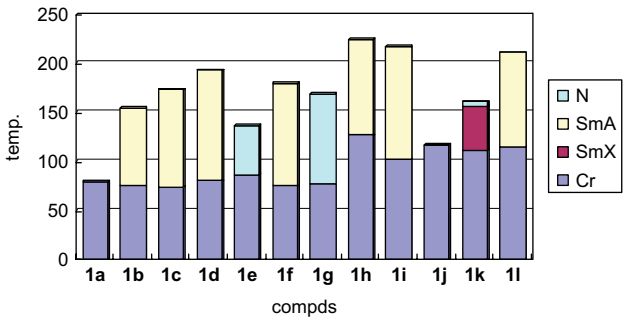


Figure 2. Bar graph showing the phase behavior of compounds **1a**–**1l**.

a transition of crystal-to-isotropic at 130.7 °C was observed. The lack of mesomorphic properties might result from the intermolecular H-bonds formed, which can lead to a stronger molecular interaction between the molecules. Figure 2 showed the bar graph of the transition temperatures of compounds **1a**–**1l**. The relationship between the melting temperatures, the clearing temperatures or the temperature ranges of the mesophases with the electronic properties of the substituents was plotted. However, no linear correlation between the clearing temperature or the temperature range of mesophases with Hammett σ_p constants for the substituents was found in this system (Fig. 3).

In order to understand the effect of terminal carbon chain length on the formation of mesophase, the compounds **2a** (X=OCH_3) and **2b** (X=CN) with a carbon chain length of n=8 and 16 were also prepared and studied. The phase transitions and thermodynamic data are summarized in Table 2. The mesomorphic properties exhibited by three compounds **2a** and **1g** with different carbon chain length (n=8, 12, 16) were compared. Compounds **2a** (n=8) and **1g** (n=12) exhibited nematic phases, however, the compound **2a** with a longer carbon chain length (n=16) formed a N phase and a SmA phase. This phase behavior is expected for rod-like molecules. The melting temperature increased slightly with the carbon chain length, i.e., T_{mp}: 106.1 °C (n=8)< 108.3 °C (n=12)<112.5 °C (n=16), however, the clearing temperatures decreased with the carbon chain length, i.e., T_{cl}: 186.0 °C (n=8)>169.5 °C (n=12)>158.1 °C (n=16). The temperature range of the mesophase increased with carbon chain length, ΔT=82.9 °C (n=8)>61.2 °C>45.6 °C (n=16) (Fig. 4). Elongation of the overall molecular length by increasing the carbon length on the other side of terminal chains led to the formation of more ordered SmA phases beside for N phase at higher temperature. This can probably

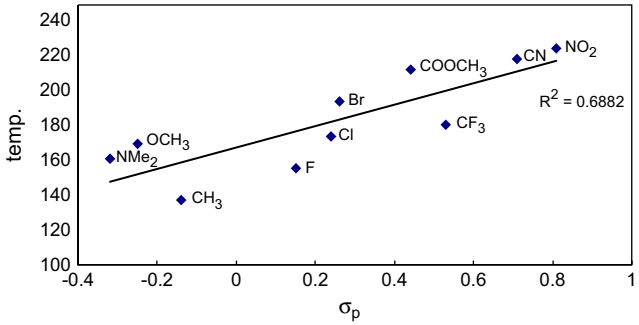


Figure 3. The plot of clearing temperature (°C) with Hammett σ_p constants of substituents in **1a**–**1l**.

Table 2. Phase transitions and enthalpies of compounds **1g**, **1i**, **2a**, and **2b**

2a;	$n=8$			Cr	106.1 (43.6) / 78.0 (42.2)	N	186.0 (0.47) / 185.3 (0.46)	I		
1g;	12	Cr_1	92.0 (4.61)	Cr_2	108.3 (51.6) / 76.3 (51.5)	N	169.5 (0.49) / 169.2 (0.47)	I		
2a;	16	Cr	112.5 (63.4) / 88.3 (67.6)	SmA	154.8 (0.43) / 153.7 (0.42)	N	158.1 (0.63) / 157.0 (0.63)	I		
2b;	8	Cr	126.3 (31.9) / 106.2 (27.3)	SmA	195.0[a] / 187.0[a]	N	233.0 (0.45) / 232.2 (0.41)	I		
1i;	12	Cr_1	102.9 (8.93) / 86.3 (6.08)	Cr_2	120.7 (40.1) / 102.7 (30.7)	SmA	219.1 (3.27) / 217.3 (3.21)	I		
2b;	16			Cr	120.9 (12.2) / 100.7 (78.8)	SmA	213.7 (6.16) / 211.9 (6.09)	I		

Cr_1, Cr_2=crystalline phases, SmA=Smectic A phase, N=nematic phase, I=isotropic phase.
[a] Determined by optical microscope.

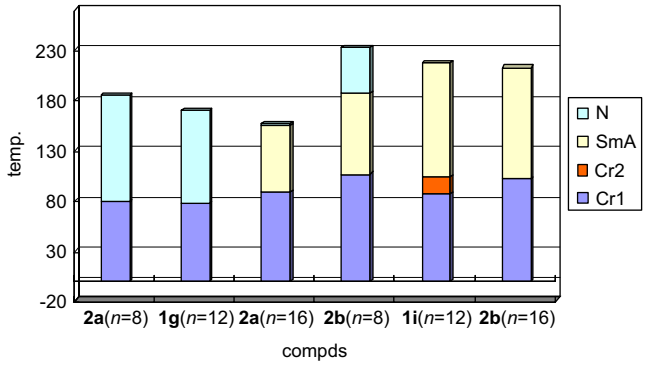
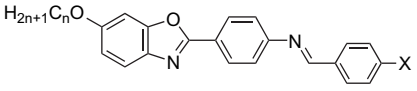


Figure 4. Bar graph showing the phase behavior of compounds **2a**, **2b**.

be attributed to an enhanced dispersive interaction between the terminal alkoxy chains. Similar mesomorphic behavior was also observed in compounds **2b** (n=8, 16) and **1i** (n=12), and compounds **2b** with longer carbon chain length (n=12, 16) favored the formation of the more ordered SmA over N phase.



n = 12
1a; X = H
1b; X = F
1c; X = Cl
1d; X = Br
1e; X = CH_3
1f; X = CF_3
1g; X = OCH_3
1h; X = NO_2
1i; X = CN
1j; X = OH
1k; X = NMe_2
1l; X = $COOCH_3$

n = 8, 16
2a; X = OCH_3
2b; X = CN

2.2. Optical properties

The UV–vis absorption and PL spectra of the compounds **1a**–**1l** in CH_2Cl_2 solution are presented in Figures 5 and 6. The data of λ_{max} peaks of UV–vis absorption and PL spectra in CH_2Cl_2 are listed in Table 3. The absorption and emission spectra of all compounds **1a**–**1l** were very similar in shape because of their structural similarity. The highest absorption peaks of all compounds were found to be insensitive to the substituents. Interestingly, they all occurred at ca. 348–365 nm except for two compounds **1h** and **1k**, for which

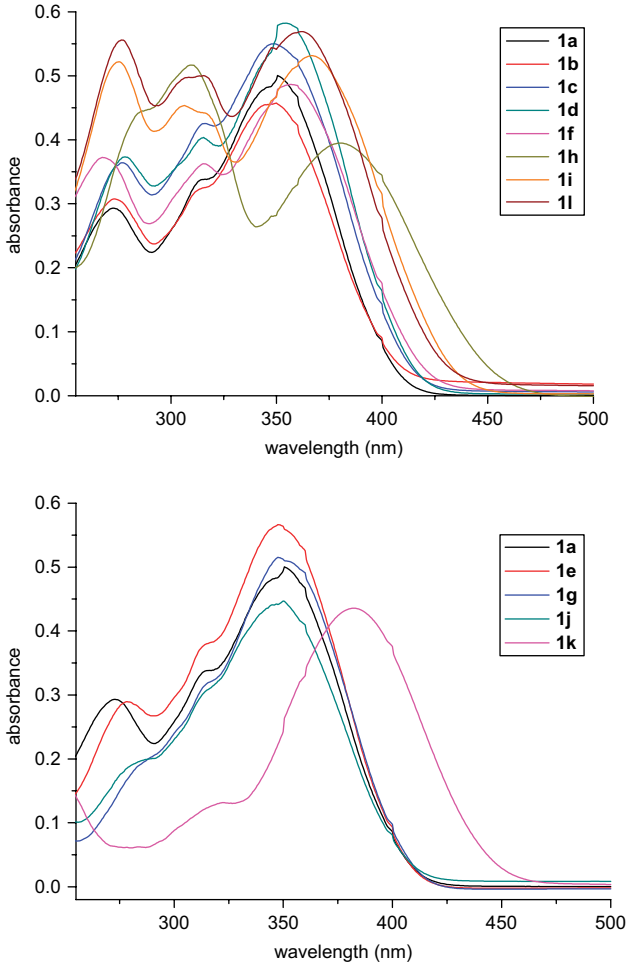


Figure 5. Normalized absorption spectra of compounds with electron-withdrawing (top) and electron-donating substituents (bottom) in CH_2Cl_2.

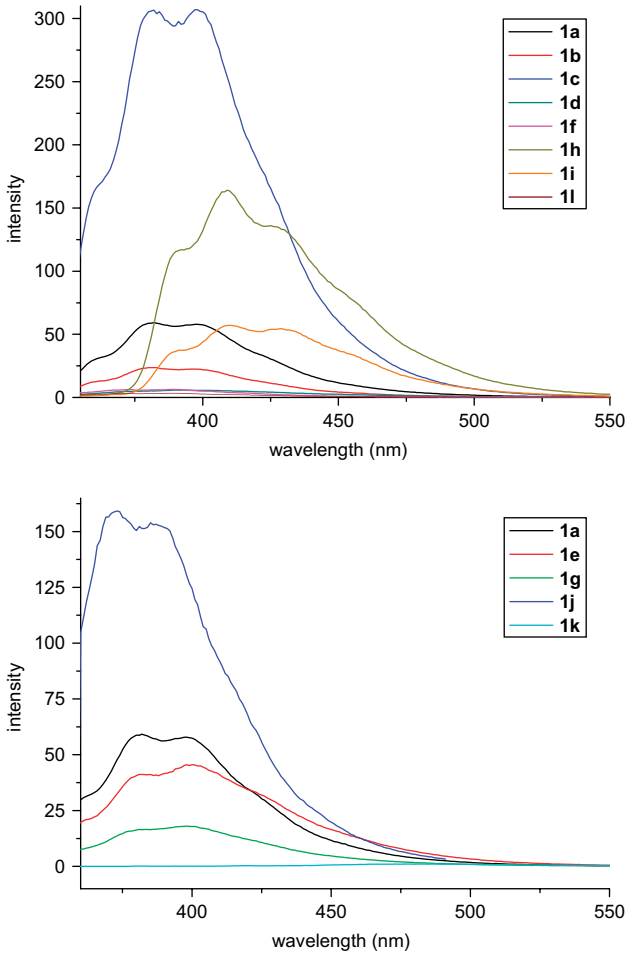


Figure 6. Normalized PL spectra of compounds with electron-withdrawing (top) and electron-donating substituents (bottom) in CH_2Cl_2.

the λ_{max} were all shifted to longer wavelength, by ca. 31 and 33 nm, respectively. The electronic properties of the substituents might not play an important role in the UV absorption spectra. The photoluminescence spectra measured in CH_2Cl_2 of compounds **1a–1l** are also shown in Figure 6. A similar trend was also observed in the photoluminescence spectra. The emission peaks occurred at 386–409 nm except for compounds **1k**, which the λ_{max} were slightly shifted to longer wavelength, by ca. 80 nm. The dependence of PL spectra is more sensitive to the electronic factor than that of UV-absorption. However, it is worth noting that the quantum yields of some compounds in CH_2Cl_2 estimated with anthracene as a standard (φ_f=0.27 in hexane) were relatively low. For example, the yields were all ranged between 0.05 and 0.07%.

Table 3. A summary of UV and PL peaks for compounds **1a–1l**

Compounds	σ_p	UV (nm)	PL (nm)
1a	0	273, 313 (sh), 348	382, 398
1b	0.15	273, 313 (sh), 348	382, 398
1c	0.24	277, 313 (sh), 348	387, 397
1d	0.26	277, 313, 352	392
1f	0.53	267, 313, 356	372, 389
1h	0.81	283 (sh), 309, 379	391 (sh), 409, 425 (sh)
1i	0.71	273, 309, 365	391 (sh), 409, 425
1l	0.44	273, 309, 362	372, 389
1e	−0.14	280, 313 (sh), 348	382, 398
1j	−0.22	280 (sh), 313 (sh), 348	372, 386
1g	−0.25	284 (sh), 313 (sh), 348	382, 398
1k	−0.32	319 (sh), 381	478

3. Conclusions

The effect of polar substituents on a series of heterocyclic benzoxazoles was systematically studied, and the formation of mesophases was observed depending on the electronic and/or the steric factors of the substituents. In general, the mesophase observed was improved by introducing a polar group. Most compounds (except **1j**) exhibited nematic or smectic A phases. Compounds with electron-donating substituents favored nematic phases, however, compounds with electron-withdrawing substituents formed smectic A phases. However, no linear correlation between the clearing temperature or the temperature range of mesophases with Hammett σ_p constants was found.

4. Experimental section

4.1. General

All chemicals and solvents were reagent grades from Lancaster or Aldrich. Solvents were dried by standard techniques. ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300. FTIR spectra were performed on Nicolet Magna-IR 550 spectrometer. DSC thermographs were carried out on a Mettler DSC 821 and calibrated with a pure indium sample (mp=156.60 °C, 28.45 J/K), and all phase transitions are determined by a scan rate of 10.0°/min. Optical polarized microscopy was carried out on an Zeiss AxiaPlan equipped with a hot stage system of Mettler FP90/FP82HT. The UV–vis absorption and fluorescence spectra were obtained using HITACHI F-4500 or JASCO V-530 spectrometer, and all spectra were recorded at room temperature. Elemental analysis for carbon, hydrogen, and nitrogen were conducted on a Heraeus Vario EL-III elemental analyzer at National Taiwan University.

3-Alkoxyphenols, 5-alkoxy-2-nitrophenols, 2-amino-5-alkoxyphenols, 5-alkoxy-2-[(4-nitro-benzylidene)amino]-phenols, 6-alkoxy-2-(4-nitrophenyl)benzoxazoles, 4-(6-alkoxybenzoxazol-2-yl)phenylamines were prepared by similar procedures.[5a]

4.1.1. 3-Dodecyloxyphenol[5a] (*n*=12). White solid, yield 60%. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.43 (m, 18H, $-CH_2$), 1.72–1.77 (m, 2H, $-OCH_2CH_2$), 3.90 (t, 2H, $-OCH_2$, J=6.6 Hz), 6.39–6.40 (m, 2H, Ar-H), 6.46–6.48 (m, 1H, Ar-H), 7.10 (t, 1H, Ar-H, J=8.5 Hz). ^{13}C NMR ($CDCl_3$): δ 14.14, 22.71, 26.05, 29.23, 29.37, 29.42, 29.60, 29.63, 29.66, 29.68, 31.94, 68.10, 102.08, 107.10, 107.59, 130.10, 156.68, 160.51.

4.1.2. 5-Dodecyloxy-2-nitrophenol[5a] (*n*=12). Yellow solid, yield 25%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.24–1.44 (m, 18H, $-CH_2$), 1.75–1.80 (m, 2H, $-CH_2$), 3.99 (t, 2H, $-OCH_2$, J=6.5 Hz), 6.47–6.49 (m, 2H, Ar-H), 8.00 (d, 1H, Ar-H, J=10.1 Hz), 11.02 (s, 1H,

Ar-OH). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.69, 25.87, 28.83, 29.27, 29.35, 29.41, 29.52, 29.57, 29.63, 29.64, 29.71, 31.92, 69.15, 101.80, 109.83, 126.91, 127.54, 158.01, 166.74.

4.1.3. 2-Amino-5-dodecyloxyphenol[5a] (n=12). White solid, yield 85%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.24–1.41 (m, 18H, –CH_2), 1.68–1.73 (m, 2H, –CH_2), 3.84 (t, 2H, –OCH_2, J=6.6 Hz), 6.32 (dd, 1H, Ar-H, J=2.6 Hz, 8.6 Hz), 6.41 (d, 1H, Ar-H, J=2.7 Hz), 6.75 (d, 1H, Ar-H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$): δ 13.94, 22.59, 26.02, 29.25, 29.34, 29.51, 29.53, 29.56, 29.58, 31.85, 68.67, 102.72, 106.75, 120.85, 125.58, 148.06, 154.94.

4.1.4. 5-Dodecyloxy-2-[(4-nitrobenzylidene)amino]phenol[5a] (n=12). Orange solid, yield 90%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.8 Hz), 1.25–1.44 (m, 18H, –CH_2), 1.74–1.79 (m, 2H, –CH_2), 3.94 (t, 2H, –OCH_2, J=6.5 Hz), 6.47 (dd, 1H, Ar-H, J=2.4 Hz, 8.9 Hz), 6.55 (d, 1H, Ar-H, J=2.5 Hz), 7.31 (d, 1H, Ar-H, J=8.9 Hz), 7.40 (s, 1H, Ar-OH), 7.99 (d, 2H, Ar-H, J=8.6 Hz), 8.29 (d, 2H, Ar-H, J=8.6 Hz), 8.66 (s, 1H, Ar–CH=N–Ar). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.70, 26.02, 29.16, 29.36, 29.38, 29.58, 29.60, 29.65, 29.67, 31.93, 68.39, 100.57, 107.84, 116.45, 124.11, 127.46, 128.73, 141.71, 148.90, 149.83, 154.66, 161.56.

4.1.5. 6-Dodecyloxy-2-(4-nitrophenyl)benzoxazole[5a] (3; n=12). The mixture of 5-dodecyloxy-2-[(4-nitrobenzylidene)amino]phenol (3.2 g, 0.007 mol) dissolved in 125 mL of CH_2Cl_2 and $Pb(OAc)_4$ (4.32 g, 0.01 mol) was refluxed for 4 h. The solution was extracted with 100 mL of CH_2Cl_2/H_2O (1/2), and the organic layers were combined and dried over $MgSO_4$. The solution was concentrated and the brown solids were recrystallized from C_2H_5OH. The light yellow solids were isolated with a yield of 85%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.25–1.49 (m, 18H, –CH_2), 1.74–1.84 (m, 2H, –CH_2), 4.01 (t, 2H, –OCH_2, J=6.5 Hz), 6.99 (dd, 1H, Ar-H, J=2.28, 8.8 Hz), 7.09 (d, 1H, Ar-H, J=2.2 Hz), 7.65 (d, 1H, Ar-H, J=8.8 Hz), 8.34 (m, 4H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.69, 26.05, 29.18, 29.35, 29.39, 29.58, 29.60, 29.64, 29.66, 31.92, 68.95, 95.92, 114.39, 120.67, 124.21, 127.82, 133.04, 135.61, 149.01, 152.07, 158.79, 159.70.

4.1.6. 4-(6-Dodecyloxybenzoxazol-2-yl)phenylamine[5a] (4; n=12). To a solution of 6-dodecyloxy-2-(4-nitrophenyl)-benzoxazole (2.54 g, 0.006 mol) dissolved in absolute C_2H_5OH (100 mL) was added powdered Pd/C (0.1 g, 0.001 mol) under nitrogen atmosphere. The solution was gently refluxed for 10 min and then N_2H_4 (0.36 g, 0.007 mol) was added. The mixture was refluxed for 6 h. The solution was filtered while hot. The filtrate was concentrated to give off-white solids. The products isolated as white solids were obtained after recrystallization from C_2H_5OH, yield 80%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.22–1.46 (m, 18H, –CH_2), 1.78–1.81 (m, 2H, –CH_2), 3.98 (t, 2H, –OCH_2, J=6.6 Hz), 6.73 (dd, 2H, Ar-H, J=1.57, 6.9 Hz), 6.88 (dd, 1H, Ar-H, J=2.31, 8.7 Hz), 7.04 (d, 1H, Ar-H, J=2.3 Hz), 7.53 (d, 1H, Ar-H, J=8.7 Hz), 7.97 (d, 2H, Ar-H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$): δ 14.15, 22.71, 26.08, 29.28, 29.37, 29.43, 29.60, 29.62, 29.66, 29.68, 31.94, 68.88, 96.13, 112.74, 114.70, 117.27, 119.17, 128.93, 135.96, 149.26, 151.35, 157.19, 162.94.

4.1.7. Benzylidene-4-(6-dodecyloxybenzoxazol-2-yl)phenylamine (1a; n=12, X=H). A mixture of benzaldehyde (0.10 mL, 0.001 mol) and 4-(6-dodecyloxybenzoxazol-2-yl)phenylamine (0.4 g, 0.001 mol) was dissolved in 100 mL of absolute ethanol under nitrogen atmosphere. The solution was refluxed for 10 min, and 0.5 mL of acetic acid was slowly added. The solution was refluxed for 12 h. The brown solids were then collected. The products isolated as light yellow solids were obtained after recrystallization from C_2H_5OH, yield 78%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.8 Hz), 1.25–1.47 (m, 18H, –CH_2), 1.80–1.83 (m, 2H, –CH_2), 4.00 (t, 2H, –OCH_2, J=6.6 Hz), 6.94 (dd, 1H, Ar-H, J=2.3 Hz, 8.7 Hz), 7.09 (d, 1H, Ar-H, J=2.3 Hz), 7.31 (d, 2H, Ar-H, J=8.4 Hz), 7.47–7.50 (m, 3H, Ar-H), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.91–7.92 (m, 2H, Ar-H), 8.21 (d, 2H, Ar-H, J=8.5 Hz), 8.49 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.08, 29.26, 29.36, 29.42, 29.60, 29.62, 29.66, 29.68, 31.94, 68.90, 96.08, 113.33, 119.81, 121.44, 124.88, 128.29, 128.87, 129.04, 131.81, 135.86, 135.94, 151.67, 154.42, 157.78, 161.20, 162.04. IR (KBr): 2919, 2848, 1625, 1614, 1505, 1496, 1490, 1467, 1281, 1226, 1150, 1053, 1004, 968, 861, 840, 800 cm^{-1}. MS (FAB): calcd for $C_{32}H_{39}N_2O_2$: 482.3, found: 483.4 $[M+H]^+$. Anal. Calcd for $C_{32}H_{38}N_2O_2$: C, 79.61; H, 7.79; N, 5.42. Found: C, 79.63; H, 7.94; N, 5.80.

4.1.8. 4-(6-Dodecyloxybenzoxazol-2-yl)phenyl-(4-fluorobenzylidene)amine (1b; n=12, X=F). Light yellow solid, yield 81%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.25–1.48 (m, 18H, –CH_2), 1.79–1.82 (m, 2H, –CH_2), 3.99 (t, 2H, –OCH_2, J=6.7 Hz), 6.93 (dd, 1H, Ar-H, J=2.3 Hz, 8.70 Hz), 7.07 (d, 1H, Ar-H, J=2.2 Hz), 7.16 (t, 2H, Ar-H, J=8.6 Hz), 7.29 (d, 2H, Ar-H, J=8.5 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.91 (dd, 2H, Ar-H, J=5.6, 8.6 Hz), 8.20 (d, 2H, Ar-H, J=8.5 Hz), 8.44 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.25, 29.36, 29.42, 29.59, 29.61, 29.65, 29.67, 31.93, 68.91, 96.09, 113.35, 115.99, 116.16, 119.81, 121.41, 124.96, 128.30, 131.02, 131.09, 132.31, 132.33, 135.85, 151.67, 154.15, 157.81, 159.58, 161.98, 163.95, 165.97. MS (FAB): calcd for $C_{32}H_{38}FN_2O_2$: 500.3, found: 501.4 $[M+H]^+$. Anal. Calcd for $C_{32}H_{37}FN_2O_2$: C, 76.77; H, 7.45; N, 5.60. Found: C, 76.48; H, 7.59; N, 5.45.

4.1.9. 4-Chlorobenzylidene-4-(6-dodecyloxybenzoxazol-2-yl)phenylamine (1c; n=12, X=Cl). Light yellow solid, yield 84%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.8 Hz), 1.25–1.48 (m, 18H, –CH_2), 1.79–1.82 (m, 2H, –CH_2), 4.00 (t, 2H, –OCH_2, J=6.6 Hz), 6.94 (dd, 1H, Ar-H, J=2.29, 8.7 Hz), 7.08 (d, 1H, Ar-H, J=2.2 Hz), 7.30 (t, 2H, Ar-H, J=8.5 Hz), 7.45 (d, 2H, Ar-H, J=8.4 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.85 (d, 2H, Ar-H, J=8.4 Hz), 8.21 (d, 2H, Ar-H, J=8.4 Hz), 8.45 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.25, 29.36, 29.42, 29.59, 29.62, 29.65, 29.68, 31.93, 68.90, 96.08, 113.37, 114.69, 119.83, 121.43, 125.12, 128.30, 128.92, 129.19, 130.16, 134.43, 135.84, 137.86, 151.68, 153.96, 157.82, 159.60, 161.93. IR (KBr): 2918, 2852, 1612, 1503, 1489,

1472, 1361, 1321, 1230, 1223, 1148, 1052, 1011, 973, 852, 815 cm^{-1}. MS (FAB): calcd for $C_{32}H_{38}ClN_2O_2$: 516.3, found: 517.3 $[M+H]^+$. Anal. Calcd for $C_{32}H_{37}ClN_2O_2$: C, 74.33; H, 7.21; N, 5.42. Found: C, 74.35; H, 7.40; N, 5.31.

4.1.10. 4-Bromobenzylidene-4-(6-dodecyloxybenzoxazol-2-yl)phenylamine (1d; *n*=12, X=Br). Light yellow solid, yield 83%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.79–1.84 (m, 2H, $-CH_2$), 4.00 (t, 2H, $-OCH_2$, J=6.6 Hz), 6.94 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.30 (d, 2H, Ar-H, J=8.5 Hz), 7.59–7.62 (m, 3H, Ar-H), 7.78 (d, 2H, Ar-H, J=8.4 Hz), 8.21 (d, 2H, Ar-H, J=8.5 Hz), 8.43 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.25, 29.36, 29.41, 29.59, 29.61, 29.65, 29.67, 31.93, 68.91, 96.08, 119.83, 121.42, 125.15, 126.41, 128.31, 130.34, 132.16, 134.83, 135.84, 151.68, 153.94, 157.83, 159.73, 161.93. IR (KBr): 2915, 2848, 1625, 1612, 1583, 1566, 1487, 1470, 1397, 1320, 1299, 1219, 1147, 1114, 1068, 1054, 1009, 847, 820 cm^{-1}. MS (FAB): calcd for $C_{32}H_{38}BrN_2O_2$: 560.2, found: 561.2 $[M+H]^+$. Anal. Calcd for $C_{32}H_{37}BrN_2O_2$: C, 68.44; H, 6.64; N, 4.99. Found: C, 68.67; H, 6.63; N, 4.73.

4.1.11. 4-(6-Dodecyloxybenzoxazol-2-yl)phenyl-(4-methylbenzylidene)amine (1e; *n*=12, X=CH_3). Light yellow solid, yield 82%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.7 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.79–1.82 (m, 2H, $-OCH_2CH_2$), 2.41 (s, 3H, Ar-CH_3), 3.99 (t, 2H, $-OCH_2$, J=6.5 Hz), 6.93 (dd, 1H, Ar-H, J=2.0, 8.65 Hz), 7.07 (d, 1H, Ar-H, J=1.9 Hz), 7.27–7.30 (m, 4H, Ar-H), 7.60 (d, 2H, Ar-H, J=8.7 Hz), 7.80 (d, 2H, Ar-H, J=7.9 Hz), 8.20 (d, 2H, Ar-H, J=8.4 Hz), 8.44 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.14, 21.70, 22.71, 26.08, 29.26, 29.37, 29.42, 29.60, 29.62, 29.66, 29.68, 31.94, 68.89, 96.07, 113.30, 119.78, 121.46, 124.67, 128.27, 129.05, 129.62, 133.40, 135.86, 142.42, 151.66, 154.62, 157.75, 161.14, 162.10. IR (KBr): 2919, 2848, 1628, 1507, 1489, 1466, 1347, 1282, 1227, 1152, 1137, 1052, 1008, 969, 861, 844, 810, 800 cm^{-1}. MS (FAB): calcd for $C_{32}H_{41}N_2O_2$: 496.3, found: 497.3 $[M+H]^+$. Anal. Calcd for $C_{32}H_{40}N_2O_2$: C, 79.80; H, 8.12; N, 5.64. Found: C, 79.84; H, 8.57; N, 5.30.

4.1.12. 4-(6-Dodecyloxybenzoxazol-2-yl)phenyl-(4-trifluoromethylbenzylidene)amine (1f; *n*=12, X=CF_3). Light yellow solid, yield 85%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.79–1.82 (m, 2H, $-CH_2$), 3.99 (t, 2H, $-OCH_2$, J=6.5 Hz), 6.94 (dd, 1H, Ar-H, J=2.20, 8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.1 Hz), 7.32 (d, 2H, Ar-H, J=8.4 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.73 (d, 2H, Ar-H, J=8.1 Hz), 8.02 (d, 2H, Ar-H, J=8.0 Hz), 8.22 (d, 2H, Ar-H, J=8.5 Hz), 8.52 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.25, 29.37, 29.42, 29.60, 29.62, 29.66, 29.68, 31.94, 68.89, 96.05, 113.41, 119.87, 121.47, 122.75, 124.91, 125.48, 125.80, 125.83, 128.32, 129.17, 132.97, 133.23, 135.80, 138.95, 151.69, 153.57, 157.87, 159.37, 161.82. IR (KBr): 2918, 2849, 1623, 1610, 1575, 1487, 1470, 1361, 1332, 1299, 1225, 1178, 1169, 1148, 1131, 1106, 1069, 1014, 860, 842, 816 cm^{-1}. MS (FAB): calcd for $C_{33}H_{38}F_3N_2O_2$: 550.3, found: 551.3 $[M+H]^+$. Anal. Calcd for $C_{33}H_{37}F_3N_2O_2$: C, 71.78; H, 6.59; N, 4.82. Found: C, 71.98; H, 6.77; N, 5.09.

4.1.13. 4-(6-Dodecyloxybenzoxazol-2-yl)phenyl-(4-methoxybenzylidene)amine (1g; *n*=12, X=OCH_3). Light yellow solid, yield 82%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.77–1.83 (m, 2H, $-CH_2$), 3.86 (s, 3H, Ar-OCH_3), 3.99 (t, 2H, $-OCH_2$, J=6.5 Hz), 6.93 (dd, 1H, Ar-H, J=2.4, 8.7 Hz), 6.98 (d, 2H, Ar-H, J=8.8 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.28 (d, 2H, Ar-H, J=7.0 Hz), 7.59 (d, 1H, Ar-H, J=8.70 Hz), 7.85 (d, 2H, Ar-H, J=8.73 Hz), 8.19 (d, 2H, Ar-H, J=8.53 Hz), 8.40 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.08, 29.26, 29.36, 29.42, 29.60, 29.62, 29.66, 29.68, 31.93, 55.47, 68.90, 96.08, 113.28, 114.30, 119.75, 121.46, 124.48, 128.27, 128.99, 130.82, 135.88, 151.66, 154.74, 157.73, 160.43, 162.15, 162.61. IR (KBr): 2920, 2852, 1607, 1591, 1574, 1511, 1488, 1470, 1320, 1301, 1256, 1223, 1172, 1148, 1052, 1029, 1005, 860, 836, 815 cm^{-1}. MS (FAB): calcd for $C_{33}H_{41}N_2O_3$: 512.3, found: 513.4 $[M+H]^+$. Anal. Calcd for $C_{33}H_{40}N_2O_3$: C, 77.14; H, 7.59; N, 5.20. Found: C, 77.31; H, 7.86; N, 5.46.

4.1.14. [4-(6-Dodecyloxybenzoxazol-2-yl)phenyl]-(4-nitrobenzylidene)amine (1h; *n*=12, X=NO_2). Bright yellow solid, yield 85%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.79–1.86 (m, 2H, $-CH_2$), 4.00 (t, 2H, $-OCH_2$–, J=6.6 Hz), 6.94 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.35 (d, 2H, Ar-H, J=8.5 Hz), 7.61 (d, 1H, Ar-H, J=8.7 Hz), 8.08 (d, 2H, Ar-H, J=8.8 Hz), 8.24 (d, 2H, Ar-H, J=8.5 Hz), 8.33 (d, 2H, Ar-H, J=8.7 Hz), 8.58 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.70, 26.07, 29.24, 29.36, 29.41, 29.59, 29.61, 29.65, 29.67, 31.93, 68.92, 96.08, 113.49, 119.93, 121.54, 124.10, 125.95, 128.37, 129.63, 135.79, 141.22, 149.53, 151.72, 153.09, 157.95, 158.24, 161.68. IR (KBr): 2925, 2848, 1714, 1680, 1623, 1611, 1583, 1574, 1551, 1488, 1471, 1362, 1345, 1323, 1284, 1221, 1150, 1113, 1004, 971, 858, 846, 828 cm^{-1}. MS (FAB): calcd for $C_{32}H_{38}N_3O_4$: 527.3, found: 528.3 $[M+H]^+$. Anal. Calcd for $C_{32}H_{37}N_3O_4$: C, 72.84; H, 7.07; N, 7.96. Found: C, 73.01; H, 6.99; N, 7.81.

4.1.15. 4-{[4-(6-Dodecyloxybenzoxazol-2-yl)phenylimino]methyl}benzonitrile (1i; *n*=12, X=CN). Light yellow solid, yield 86%. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, $-CH_3$, J=6.9 Hz), 1.25–1.48 (m, 18H, $-CH_2$), 1.80–1.83 (m, 2H, $-CH_2$), 4.00 (t, 2H, $-OCH_2$, J=6.6 Hz), 6.93 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.08 (d, 1H, Ar-H, J=2.3 Hz), 7.29 (d, 2H, Ar-H, J=9.6 Hz), 7.59–7.62 (m, 3H, Ar-H), 7.77 (d, 2H, Ar-H, J=8.4 Hz), 8.21 (d, 2H, Ar-H, J=8.5 Hz), 8.43 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.24, 29.36, 29.41, 29.59, 29.61, 29.65, 29.67, 31.93, 68.92, 96.08, 113.47, 114.82, 118.35, 119.91, 121.50, 125.81, 128.36, 129.30, 132.62, 135.80, 139.63, 151.71, 153.21, 157.93, 158.73, 161.72. IR (KBr): 2921, 2849, 1714, 1681, 1626, 1613, 1495, 1488, 1467, 1361, 1281, 1223, 1152, 1135, 1050, 1010, 971, 861, 847, 799 cm^{-1}. MS (FAB): calcd for $C_{33}H_{38}N_3O_2$: 507.3, found: 508.3 $[M+H]^+$. Anal. Calcd for $C_{33}H_{37}N_3O_2$: C, 78.07; H, 7.35; N, 8.28. Found: C, 78.04; H, 7.23; N, 8.27.

4.1.16. [4-(6-Dodecyloxybenzoxazol-2-yl)phenyl]-(4-dimethylaminebenzylidene)amine (1k; n=12, X=NMe_2). Yellow solid, yield 85%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.25–1.48 (m, 18H, –CH_2), 1.79–1.82 (m, 2H, –CH_2), 3.05 (s, 6H, –NMe_2), 3.99 (t, 2H, –OCH_2, J=6.6 Hz), 6.72 (d, 2H, Ar-H, J=8.9 Hz), 6.92 (dd, 1H, Ar-H, J=2.3, 8.70 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.28 (d, 2H, Ar-H, J=8.4 Hz), 7.59 (d, 1H, Ar-H, J=8.7 Hz), 7.77 (d, 2H, Ar-H, J=8.5 Hz), 8.18 (d, 2H, Ar-H, J=8.5 Hz), 8.34 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.14, 22.71, 26.08, 29.27, 29.37, 29.43, 29.60, 29.62, 29.66, 29.68, 31.94, 40.16, 68.89, 96.08, 111.56, 113.19, 119.68, 121.54, 123.86, 124.04, 128.24, 130.84, 135.94, 151.64, 152.79, 155.36, 157.64, 160.84, 162.36. IR (KBr): 2920, 2846, 1626, 1609, 1583, 1552, 1527, 1489, 1470, 1434, 1415, 1361, 1283, 1225, 1178, 1164, 1152, 1131, 1045, 1018, 1008, 941, 862, 839, 816 cm^{-1}. MS (FAB): calcd for $C_{34}H_{44}N_3O_2$: 525.3, found: 526.4 $[M+H]^+$. Anal. Calcd for $C_{34}H_{43}N_3O_2$: C, 77.68; H, 8.24; N, 7.99. Found: C, 77.63; H, 8.39; N, 8.31.

4.1.17. 4-{[4-(6-Dodecyloxybenzoxazol-2-yl)phenylimino]methyl}benzoic acid methyl ester (1l; n=12, X=$COOCH_3$). Light yellow solid, yield 78%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.25–1.46 (m, 18H, –CH_2), 1.79–1.82 (m, 2H, –CH_2), 3.93 (s, 3H, Ar–$COOCH_3$–), 3.99 (t, 2H, –OCH_2, J=6.6 Hz), 6.93 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.32 (d, 2H, Ar-H, J=8.5 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.97 (d, 2H, Ar-H, J=8.3 Hz), 8.13 (d, 2H, Ar-H, J=8.3 Hz), 8.21 (d, 2H, Ar-H, J=8.5 Hz), 8.53 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.14, 22.70, 26.07, 29.25, 29.37, 29.42, 29.60, 29.62, 29.66, 29.68, 31.93, 52.39, 68.89, 96.05, 113.40, 119.86, 121.49, 125.39, 128.85, 130.05, 132.68, 135.81, 139.66, 151.68, 153.76, 157.85, 159.92, 161.86, 166.51. IR (KBr): 2954, 2919, 2847, 1717, 1626, 1489, 1466, 1434, 1347, 1285, 1226, 1152, 1136, 1115, 1052, 1010, 968, 957, 854, 841, 800 cm^{-1}. MS (FAB): calcd for $C_{34}H_{41}N_2O_4$: 540.3, found: 541.3 $[M+H]^+$. Anal. Calcd for $C_{34}H_{40}N_2O_4$: C, 75.53; H, 7.46; N, 5.18. Found: C, 75.36; H, 7.35; N, 4.90.

4.1.18. (4-Methoxybenzylidene)-[4-(6-octyloxybenzoxazol-2-yl)phenyl]amine (2a; n=8, X=OCH_3). Light yellow solid, yield 77%. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3H, –CH_3, J=6.9 Hz), 1.28–1.47 (m, 10H, –CH_2), 1.79–1.82 (m, 2H, –CH_2), 3.86 (s, 3H, Ar-OCH_3), 3.99 (t, 2H, –OCH_2, J=6.5 Hz), 6.93 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 6.98 (d, 2H, Ar-H, J=8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.3 Hz), 7.28 (d, 2H, Ar-H, J=6.7 Hz), 7.59 (d, 1H, Ar-H, J=8.7 Hz), 7.85 (d, 2H, Ar-H, J=8.7 Hz), 8.19 (d, 2H, Ar-H, J=8.5 Hz), 8.40 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.67, 26.08, 29.26, 29.38, 31.83, 55.47, 68.90, 96.08, 113.28, 114.30, 119.75, 121.47, 124.48, 128.27, 128.98, 130.82, 135.88, 151.66, 154.74, 157.73, 160.44, 162.15, 162.62. Anal. Calcd for $C_{29}H_{32}N_2O_3$: C, 76.29; H, 7.06; N, 6.14. Found: C, 75.94; H, 7.20; N, 5.91.

4.1.19. [4-(6-Hexadecyloxybenzoxazol-2-yl)phenyl]-(4-methoxybenzylidene)amine (2a; n=16, X=OCH_3). Light yellow solid, yield 82%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.24–1.48 (m, 26H, –CH_2), 1.79–1.82 (m, 2H, –OCH_2), 3.87 (s, 3H, Ar-OCH_3), 3.99 (t, 2H, –OCH_2, J=6.6 Hz), 6.93 (dd, 1H, Ar-H, J=2.3, 8.71 Hz), 6.98 (d, 2H, Ar-H, J=8.7 Hz), 7.08 (d, 1H, Ar-H, J=2.3 Hz), 7.29 (d, 2H, Ar-H, J=8.5 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.86 (d, 2H, Ar-H, J=8.7 Hz), 8.19 (d, 2H, Ar-H, J=8.9 Hz), 8.41 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.08, 29.26, 29.37, 29.42, 29.60, 29.62, 29.68, 29.71, 31.94, 55.47, 68.89, 96.08, 113.28, 114.31, 119.76, 121.46, 124.51, 128.27, 128.92, 130.85, 135.89, 151.66, 157.73, 160.41, 162.14. Anal. Calcd for $C_{37}H_{48}N_2O_3$: C, 78.13; H, 8.51; N, 4.93. Found: C, 76.80; H, 8.99; N, 4.73.

4.1.20. 4-{[4-(6-Octyloxybenzoxazol-2-yl)phenylimino]methyl}benzonitrile (2b; n=8, X=CN). Light yellow solid, yield 80%. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, –CH_3, J=6.9 Hz), 1.28–1.49 (m, 10H, –CH_2), 1.78–1.83 (m, 2H, –OCH_2), 4.00 (t, 2H, –OCH_2, J=6.6 Hz), 6.94 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.08 (d, 1H, Ar-H, J=2.3 Hz), 7.33 (d, 2H, Ar-H, J=6.1 Hz), 7.61 (d, 1H, Ar-H, J=8.7 Hz), 7.77 (d, 2H, Ar-H, J=8.3 Hz), 8.02 (d, 2H, Ar-H, J=8.3 Hz), 8.23 (d, 2H, Ar-H, J=8.8 Hz), 8.53 (s, 1H, –CHN). ^{13}C NMR ($CDCl_3$): δ 14.11, 22.67, 26.08, 29.25, 29.37, 31.83, 68.92, 96.07, 113.47, 114.70, 114.83, 118.36, 119.91, 121.50, 125.81, 128.36, 129.30, 129.89, 132.63, 132.91, 135.80, 139.63, 151.72, 153.22, 157.93, 158.73, 161.72. Anal. Calcd for $C_{29}H_{29}N_3O_2$: C, 77.13; H, 6.47; N, 9.31. Found: C, 77.01; H, 6.45; N, 9.15.

4.1.21. 4-{[4-(6-Hexadecyloxybenzoxazol-2-yl)phenylimino]methyl}benzonitrile (2b; n=16, X=CN). Light yellow solid, yield 87%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, –CH_3, J=6.9 Hz), 1.24–1.48 (m, 26H, –CH_2), 1.79–1.82 (m, 2H, –OCH_2), 3.99 (t, 2H, –OCH_2, J=6.5 Hz), 6.93 (dd, 1H, Ar-H, J=2.3, 8.7 Hz), 7.07 (d, 1H, Ar-H, J=2.2 Hz), 7.32 (d, 2H, Ar-H, J=8.5 Hz), 7.60 (d, 1H, Ar-H, J=8.7 Hz), 7.75 (d, 2H, Ar-H, J=8.2 Hz), 8.00 (d, 2H, Ar-H, J=8.3 Hz), 8.22 (d, 2H, Ar-H, J=8.5 Hz), 8.50 (s, 1H, Ar-CHN). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.70, 26.07, 29.25, 29.37, 29.42, 29.59, 29.62, 29.67, 29.71, 31.94, 68.90, 96.06, 113.46, 114.79, 118.34, 119.90, 121.50, 125.79, 128.34, 129.29, 132.60, 135.78, 139.61, 151.70, 153.17, 157.92, 158.69, 161.70. Anal. Calcd for $C_{37}H_{45}N_3O_2$: C, 78.83; H, 8.05; N, 7.45. Found: C, 78.83; H, 8.16; N, 7.34.

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