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Synthesis of quinoxaline–benzoxale conjugates and mesomorphic properties

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ABSTRACT

A new series of non-discotic heterocyclic compounds **1a**–**e** derived from quinoxaline was prepared and their mesomorphic properties investigated. The crystal and molecular structures of nonmesogenic 2,3-bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-butoxy2-hydroxyphenylimino)methyl] phenyl ester **2a** (n=4, m=12) were determined by means of X-ray structural analysis. It crystallizes in a monoclinic space group $P2(1)/c$, with a=21.9193(13) Å, b=8.3693(4) Å, c=30.896(2) Å, and Z=4. The molecule was considered as an elongated or tapered triangle. Both inter- and intra-molecular H-bonds were observed in the crystal lattice, which was attributed to the formation of columnar mesophase in compounds **2**. The mesomorphic behavior of compounds **1**–**2** was studied by thermal analysis and polarized optical microscopy. All compounds **1**–**2** exhibited hexagonal columnar phases (Col_h), which were also confirmed by powder XRD diffractometer. A N_{cell} and R_{ar} value equal to 4.74 and 4.34 within a slice of 9.0 Å thick were obtained for **1b** and **2b**, indicating that a more disc-like correlated structure by two molecules lying side-by-side was formed in Col_h phases. The fluorescent properties of the compounds **1**–**4** in CH_3Cl were also examined.

1. Introduction

More and more promising materials incorporating five- or six-membered heterocyclic derivatives as a core or terminal moiety have gained more impetus during the past years. Part of thus exploring motives originates from their inherent features, such as well-known chemistry/higher thermal stability, lower symmetry/non-coplanarity, electro/photoluminescence, acceptor/electron-deficiency and/or others. Quinoxalines, oxadiazoles or benzaxazole are a few prevalent examples among them, and most of these heterocyclic derivatives were often considered as electron-deficient motifs. Heteroatoms therein incorporated, such as N, S or O atom were often more polarized, therefore, a weak dipole might be possibly induced. This dipole can be intramolecularly induced within a structural moiety resulting from the other acceptor group located in two separated extremes. Similarly, an intermolecular force (D→A) between the acceptor and other donor of the neighboring molecule might be induced, giving novel electroluminescent and mesogenic properties often observed in these materials. The magnitude of the force is extremely critical in the formation of mesophases: when they are too weak or too strong the liquid crystalline behavior is then lost.

Quinoxalines were long known as highly photoluminecent and/or efficient electroluminescent materials[1] and some of them have been studied as light emitting dopants.[2] Like oxadiazoles, they were often used as electron-transporting (ETL) or hole-blocking layers in organic light-emitting diodes (OLEDs). Quinoxalines were recently also studied as dye-sensitizers used in photovoltaic or heterojunction solar cells;[3] they are relatively easy to prepare and also thermally stable. Most of these quinoxalines constructed by extended π-conjugated structures with a donor–acceptor have unique optical and electrical properties. In addition, a few luminescent iridium complexes[4] with cyclometalated[4a] or orthometalated[4b] quinoxaline ligands were reported. However, known examples of mesogenic quinoxalines[5a] or structurally similar derivatives[5b–e] were relatively lesser. A series of discotic and elliptical molecules[5e] based on dibenzophenazine carboxylic acids and their methyl ester analogs were prepared and $N/col_h/Col_r$ phases were observed. Interestingly, an enhanced mesophase range for triphenyl-based mesogens by adding 1:1 ratio with hexakis(4-nonylphenyl) dipyrazino[2,3-*f*:2′,3′-h]quinoxaline[5d] were obtained. Two new fluorescent ethyl 3-aryl-1-methyl-8-oxo-8*H*-anthra[9,1-*gh*]quinoline-2-carboxylates[5a] were synthesized, and such new dyes have shown a very good orientation parameter (S_A) in nematic liquid crystals. In contrast, known mesogenic benzoxazoles were somehow more. A few benzoxazoles[6] with structures **I**, **II**, **III** (Scheme 1) and some of their metal complexes were previously prepared and studied in this group, and their mesomorphic

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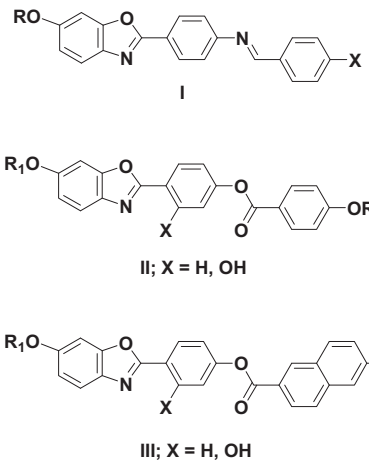
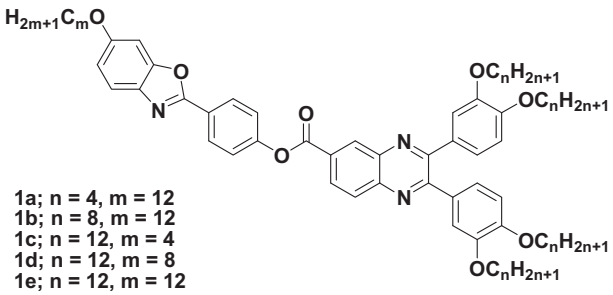
properties and optical properties investigated. All these related benzoxazoles formed SmC, SmA and/or N phases, as expected for rod-like molecules.



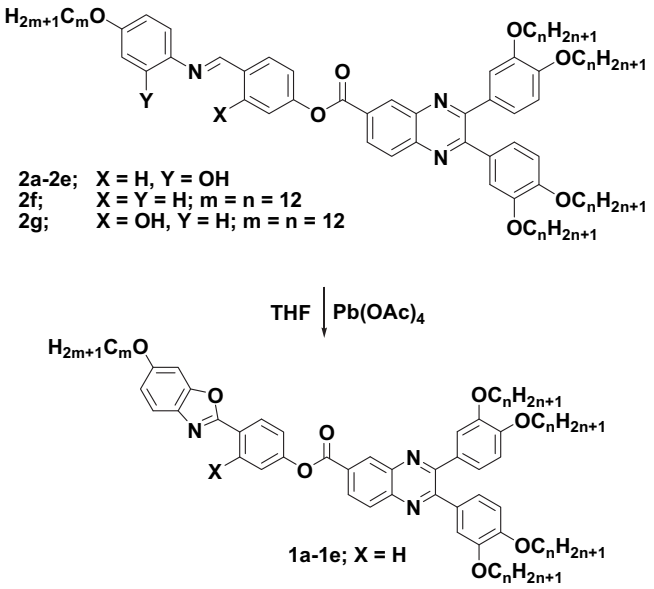
Scheme 1. The structures of mesogenic benzoxazoles **I**, **II**, and **III**.

Discotic organic molecules, particularly for those molecules with an extended π-conjugated structure have been extensively studied due to their promising materials in optoelectronic devices,[7] such as organic field-effect transistors (OFETs),[8] organic light-emitting diodes (OLEDs), and photovoltaic cells.[9] In liquid crystals, columnar phases could be generated by typical discotic or round molecules with at least a total number of six or eight side chains. However, many other types of non-discotic molecules could also form columnar phases. These are examples of half-disc, catenar/lathy,[10] cone/bowlike and bent/banana-shaped[11] molecules. In general, these compounds were often constructed with a lesser number of peripheral side chains attached around rigid core. Kinetically stable columnar phase induced by a single molecule were not easily approached by these non-discotic molecules due to their shape effect. On the other hand, lesser side chains are not able to stabilize the rigid core. Thus tuning the intermolecular interaction or using complementary shapes between molecules within the columns to generate better correlated organizations becomes a true challenge in generating such non-classical columnar liquid crystals. Among them covalent H-bond and/or π–π stacking interaction are used the most to induce such correlated mesogens or metallomesogens.

In this work, a new type of non-discotic heterocyclic compounds **1**–**2** derived from quinoxalines and benzoxales linked with an ester spacer group was prepared and their mesomorphic properties investigated. Both compounds **1b**–**d** (Scheme 2) and **2b**–**g** (Scheme 3) formed hexagonal columnar phases (Col_h), which were characterized and identified by DSC and POM and also confirmed by powder XRD. Single crystallographic data of **2a** (n=4, m=12) indicated that



Scheme 2. The structures of compounds **1a**–**e**.



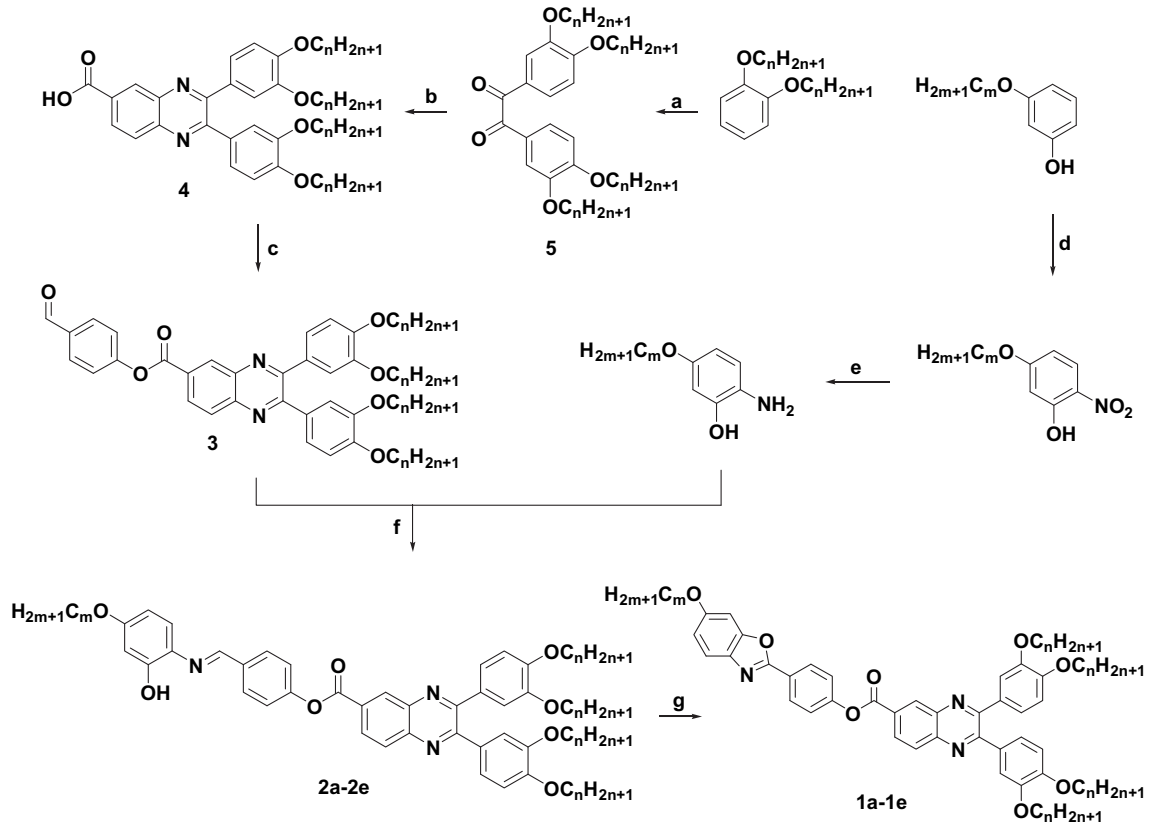
Scheme 3. The synthetic preparation of compounds **1a**–**e**.

both inter- and intra-molecular H-bonds were observed in the crystal lattice, and two molecules were arranged above and below by a head-to-tail style. A more correlated structure was organized by these H-bonds and a mesophase was then better induced. All compounds **2** have a wider temperature range of columnar phase than those of compounds **1**, which might be due to the existent H-bond in compounds **2**. Also indicated by single crystallographic data, this type of molecules has a relatively lower symmetry element. Some of these compounds, with a lower fluidity observed under polarized optical microscope were considered as room temperature liquid crystals.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic procedures for final compounds **1** are summarized in Scheme 4. 1,2-Bis(3,4-dialkoxyphenyl)-1,2-ethanediones **5** were obtained by the reaction of 1,2-dialkoxy benzenes with oxalyl chloride in the presence of $AlCl_3$ stirring in carbon disulfide at ice bath temperature, which were then condensed with 3,4-diaminobenzoic acid stirring in absolute ethanol to gave 2,3-bis-(3,4-dialkoxyphenyl) quinoxaline-6-carboxylic acids **4**. However, a characteristic broad peak[12] often appeared at δ ~13.50 assigned for -COO*H* was not observed for acids **4** due to rapid exchange. This peak in other similar structures[5e] was also not observed. Then the reactions of compounds **4** with 4-hydroxybenzaldehyde with DCC and DMAP in refluxing dried THF/absolute ethanol gave 2,3-bis(3,4-dialkoxyphenyl) quinoxaline-6-carboxylic acid 4-formyl phenyl esters **3**. The condensation of compounds **3** and 2-amino-5-alkoxyphenols in refluxing ethanol led to 2,3-bis(3,4-dialkoxyphenyl) quinoxaline-6-carboxylic acid 4-[(4-alkoxy-2-hydroxyphenylimino)methyl]phenyl esters **2**. The final compounds **1**; 2,3-bis(3,4-dialkoxyphenyl)quinoxaline-6-carboxylic acid 4-(6-alkoxybenzoxazol-2-yl)phenyl esters were obtained by the reactions of compounds **2** and lead acetate, $Pb(OAc)_4$ in refluxing THF with a yield ranged from 68 to 73%. ^1H and ^{13}C NMR spectroscopy were used to characterize all intermediates. For instance, a characteristic singlet peak occurred at δ 8.62–8.64, assigned for imine-H (–C*H*=N) of compounds **2** disappeared upon formation of final products **1**. Elemental analysis was used to confirm the purity of the compounds **1**–**2**.



Scheme 4. Reagents and conditions. (a) Oxalyl chloride (0.5 equiv), $AlCl_3$, stirred in CS_2 at 0 °C 24 h; (b) 3.4-diamino benzoic acid (1.0 equiv), AcOH (drops) stirred in EtOH, 12 h; (c) 4-hydroxybenzaldehyde (1.1 equiv), DCC (1.2 equiv), DMAP (1.2 equiv), stirred in dried THF at rt; (d) HNO3 (1.1 equiv), $NaNO_2$ (0.5 equiv), refluxed in CH_2Cl_2, 24 h; (e) Pd/C (1.1 equiv), N_2H_4 (1.1 equiv), refluxed in EtOH, 24 h; (f) refluxed in abs EtOH, 8 h; (g) $Pb(OAc)_4$ (1.2 equiv), refluxed in THF, 2 h.

2.2. Single crystal structure of 2,3-bis(3,4-didodecyloxyphenyl) quinoxaline-6-carboxylic acid 4-[(4-butoxy2-hydroxy phenylimino)methyl]phenyl ester 2a ($n=4$, $m=12$)

A single crystal of the nonmesogenic compound **2a** suitable for crystallographic analysis was obtained by slow vaporization from CH_2Cl_2 at room temperature and its structure resolved. Fig. 1 shows its molecular structure with the atomic numbering schemes. Table 1 lists its crystallographic and structural refinement data for the molecule. It crystallizes in a monoclinic space group $P2(1)/c$ with a $Z=4$. The overall molecular shape of crystal **2a** was considered as an elongated or tapered triangle with quinoxaline ring as its base. The triangle has a molecular length of ca. ~39.07 Å (C32–C58 atoms) and a basal length of ca. ~13.16 Å (C43–C60 atoms). Two phenyl rings of benzylideneamine–phenol (defined by C15–C20 and C8–C13 atoms) were coplanar, however, two other benzene rings (C34–C39 and C49–C54 atoms) attached to quinoxaline ring were not coplanar, each with a dihedral angle of 35° and 46°. Four molecules were paced in a single unit cell.

Unsurprisingly, both intra-molecular and inter-molecular H-bonds were observed in the crystal lattice. Two molecules lying above and below plane were arranged in an antiparallel head-to-tail into a layer structure. An inter-molecular H-bond of H(3A)–N1 with a bond length of 2.284 Å was observed, while other H-bond lengths induced by H(3A)–O(8) and O(3)–H(3A) atoms were measured as d ~2.79 Å and 2.30 Å, respectively (Fig. 2). These inter-molecular H-bonds have apparently enhanced the molecular interaction between the layers. Also two π–π interactions as point to face were observed; one is H7A to central phenyl ring (C2–C7) with a distance of 2.9932 Å and the other one is H8 to phenyl ring with

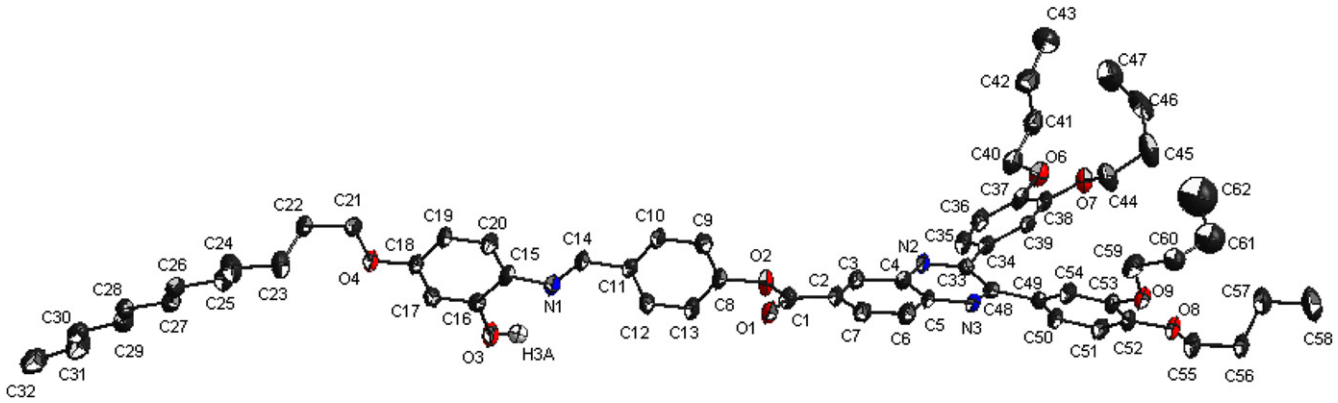


Fig. 1. An ORTEP plot for compound **2a** with the numbering scheme, and the thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 1
Crystallographic and experimental data for compound **2a**

Compd	**2a** (n=4, m=12)
Empirical formula	$C_{62}H_{79}N_3O_8$
Formula weight	994.28
T/K	150(2)
Crystal system	Monoclinic
Space group	$P2(1)/c$
a/Å	21.9193(13)
b/Å	8.3693(4)
c/Å	30.896(2)
α/°	90
β/°	97.016(2)
γ/°	90
U/Å^3	5625.4(6)
Z	4
F(000)	2144
D_c/Mg m^{-3}	1.174
Crystal size/mm^3	0.40×0.07×0.03
Range for data collection/^{0}	1.33–25.00
Reflection collected	19259
Data, restraints, parameters	9688/4/62
Independent reflection	9688 [R(int)=0.1336]
Final $R1$, $wR2$	0.0818, 0.1484

a distance of 2.669 Å. The dihedral angle between above mentioned phenyl rings was 44.71°.

2.3. Mesomorphic properties

The mesomorphic behavior of compounds **1**–**2** was studied and characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). A series of similar structures with compounds **4**, dibenzophenazine carboxylic acids[5e] and their methyl ester analogs have been prepared and studied, and an ordered hexagonal phase and an ordered rectangular/nematic phase were formed by such elliptical-shaped molecules. A dimeric structure induced by inter-molecular H-bond was attributed to the formation of mesophases in such acid derivatives.

The phase transitions and thermodynamic data for compounds **1**–**2** are summarized in Table 2. Compounds **2b**–**g** formed columnar phases based on observation under polarized microscope. Under POM, a typically pseudo focal-conic or more dendritic texture (see Fig. 3) with linear birefringent defects on slowly cooling from the isotropic liquids was clearly observed. These observed textures often accompanied by a large area of homeotropic domain are often characteristic for hexagonal columnar phases. As indicated in Table 1, all derivatives **2** exhibited enantiotropic columnar phases (Col), in which two typical transitions of crystal-to-columnar and columnar-to-isotropic (Cr→Col$_h$→I) were appeared on DSC thermographs. A few transition temperatures from Cr→Col$_h$ or Col$_h$→Cr phases for compounds **2b**, **2d**, **2e**, and **2g** were obtained from POM due to their relatively smaller enthalpies. The melting and the isotropic temperatures were ranged from T_{mp}=33.0–50.2 °C and T_{cl}=71.6–104.7 °C on heating process, and the temperature ranges of columnar phases were ranged from ΔT_{col}=31.8–54.9 °C. Compound **2e** has a slightly wider temperature of mesophase, i.e., ΔT_{col}=54.0>46.0>31.8 °C than those of compounds **2f** and **2g**, respectively. The reason for this smaller range of decreasing mesophase temperatures was uncertain, and it might be probably attributed to the intermolecular or/and intra-molecular H-bonded interaction (–OH···O). On the other hand, there might exist H-bonds in compound **2e** and **2g**, whereas no such H-bond was possible in compound **2f**.

The formation of columnar phases was often sensitive to the side-chain density, i.e., the larger size or the more rigid is the core group, and more side-chain density is necessarily required. The overall molecular shape of compounds **2** and **1** is considered as an elongated triangular shape, therefore, two molecules arranged side-by-side to adopt an overall correlated disc molecule were then proposed (see later discussion). Similar mesomorphic behavior for compounds **1** was also observed. Compound **1a** was not mesogenic, and a higher clearing temperature by 22.1 °C than that of **2a** was

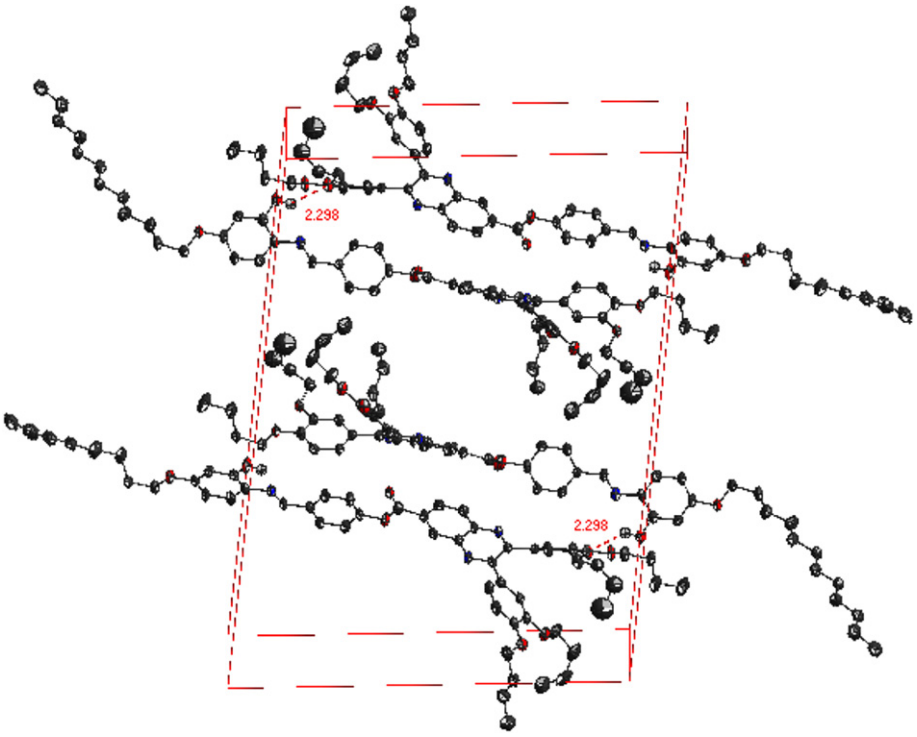


Fig. 2. Inter-molecular H-bonds in unit cell.

Table 2
The phase temperatures and enthalpies[a] of compounds **1** and **2**

2a	n = 4, m = 12		Cr_1	64.1 (10.9)	Cr_2	71.1 (17.4)	I	
						32.2[b]		
2b	8	12	Cr	44.5[b]	Col_h	85.1 (1.63)	I	
				33.9[b]		79.7 (1.47)		
2c	12	4	Cr	51.4 (17.0)	Col_h	98.6 (3.98)	I	
				30.1 (11.3)		95.3 (3.87)		
2d	12	8	Cr	50.2[b]	Col_h	104.7 (3.62)	I	
				38.2[b]		101.8 (3.56)		
2e	12	12	Cr	49.5[b]	Col_h	104.4 (3.78)	I	
				35.1[b]		101.6 (3.71)		
2f	12	12	Cr	33.3 (7.15)	Col_h	79.3 (1.81)	I	
				23.9 (6.49)		75.4 (1.68)		
2g	12	12	Cr	39.8[b]	Col_h	71.6 (1.75)	I	
				30.6[b]		62.5 (1.44)		
1a	4	12			Cr	93.2[b]	I	
						64.2[b]		
1b	8	12	Cr			47.8 (1.62)	I	
				37.0 (1.11)	Col_h	46.6[b]		
1c	12	4	Cr	45.7[b]	Col_h	79.2 (6.63)	I	
				37.4[b]		75.9 (6.58)		
1d	12	8	Cr	42.1[b]	Col_h	83.9 (4.65)	I	
				33.9[b]		80.4 (4.48)		
1e	12	12	Cr	45.8[b]	Col_h	77.1 (3.89)	I	
				40.3[b]		73.6 (3.82)		

[b]Observed by polarized microscope.
[a] Cr=crystal, Col_h=hexagonal columnar, I=isotropic phase. The temperatures (°C) and enthalpies (kJ/mol) were determined by DSC at a scan rate of 10.0 °C/min.

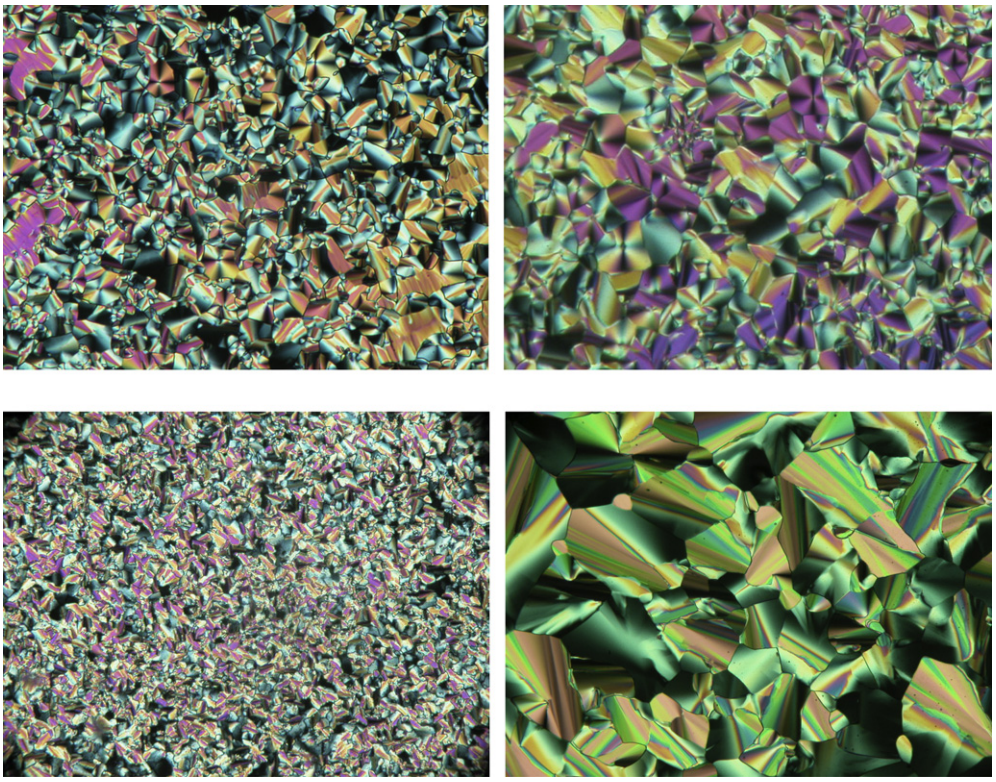


Fig. 3. Optical textures observed by compounds; **2e** at 70.0 °C (top left), **2f** at 65 °C (top right), **2g** at 50.0 °C (bottom left), and **1d** at 75.0 °C (bottom right).

obtained. All other compounds **1b**–**e** have lower melting and clearing temperatures than those of compounds **2b**–**e**. The temperature range of mesophase for **1b**–**e** was narrower than those of **2b**–**e**. Similar optical textures for **2** were also characterized under POM, and the mesophases were identified as columnar phases.

2.4. Variable-temperature powder XRD data

Variable-temperature powder XRD diffraction experiments were conducted to confirm the structure of the mesophases of compounds **1**–**2**. A summary of the diffraction peaks and lattice constants for compounds **1**–**2** is listed in Table 3. For derivatives **2b**–**g**, a typical diffraction pattern of a two-dimensional hexagonal lattice with one very strong diffraction peak at lower angle and two much weaker diffraction peaks was all observed. These are the characteristic of hexagonal columnar phases with a *d*-spacing ratio of 1, $(1/3)^{1/2}$, and $(1/4)^{1/2}$, corresponding to Miller indices; 100, 110, and 200, respectively. For example, a diffraction pattern at 90 °C with a *d*-spacing at 35.66 Å, 20.62 Å, 17.84 Å and a broad diffuse peak (4.61 Å) at wide-angle region was observed for compound **2e** and this diffraction pattern corresponded to a hexagonal columnar arrangement (see Fig. 5a). This diffraction pattern corresponds to an intercolumnar distance or lattice constant (i.e., a parameter of the hexagonal lattice) of 41.18 Å. On the other hand, a lattice constant of 38.08–41.10 Å for mesogenic **2b**–**e** were all close to the molecular length (ca. disc diameter) ~38.01 Å of nonmesogenic **2a**. The lack of any relatively peaks at wide angles excluded a more regular periodicity along the columns. However, liquid-like correlations between the rigid cores occurred at wide angle regions of 4.43–4.61 Å. The hexagonal lattices were correlated quite well with increasing side-chain alkoxy carbon lengths.

Unsurprisingly, all compounds **1b**, **1d**, and **1e** gave similar XRD diffraction patters as compounds **2b**, **2d**, and **2f** due to their similar structures. The lattice constants of compounds **1** were slightly smaller than that of compounds **2** by ca. 1.58 Å ($a_{\mathbf{2e}}$, $-a_{\mathbf{1e}}$)–3.01 Å ($a_{\mathbf{2d}}$–$a_{\mathbf{1d}}$), which might be due to a less interdigitation of alkoxy chains in compounds **1**. A few XRD diffractions of compounds **2f**, **2g**, and **1b** were shown in Fig. 4. The XRD data were also consistent with single crystallographic analysis. The molecular length was measured as ca. 39.07 Å, which was quite close to the *d*-spacing of 38.08 Å and 36.10 Å obtained by powder XRD diffraction experiment for compound **2b** and **1b**, respectively. Therefore, alkoxy side

Table 3
Variable-temperature XRD diffraction data for compounds **1**–**2**

Compd	Mesophase/temp	Lattice const./Å	*d*-Spacing/Å obs	Miller indices
2b	Col_h (70 °C)	*a*=38.08	32.98 (32.98)	100
			19.17 (19.04)	110
			16.68 (16.50)	200
			4.55 (br)	halo
2d	Col_h (90 °C)	*a*=41.20	35.68 (35.68)	100
			20.56 (20.60)	110
			17.75 (17.84)	200
			4.60 (br)	halo
2e	Col_h (90 °C)	*a*=41.18	35.66 (35.66)	100
			20.62 (20.59)	110
			17.84 (17.83)	200
			4.61 (br)	halo
2f	Col_h (65 °C)	*a*=42.45	36.76 (36.76)	100
			21.17 (21.22)	110
			18.35 (18.38)	200
			4.47 (br)	halo
1b	Col_h (41 °C)	*a*=36.10	31.26 (31.26)	100
			18.15 (18.05)	110
			15.71 (15.63)	200
			4.48 (br)	halo
1c	Col_h (70 °C)	*a*=36.49	31.60 (32.42)	100
			18.30 (18.24)	110
			15.88 (15.80)	200
			4.53 (br)	halo
1d	Col_h (76 °C)	*a*=38.19	33.07 (33.07)	100
			18.98 (19.09)	110
			16.50 (16.53)	200
			4.58 (br)	halo
1e	Col_h (68 °C)	*a*=39.60	34.29 (34.29)	100
			17.19 (17.15)	110
			4.57 (br)	halo

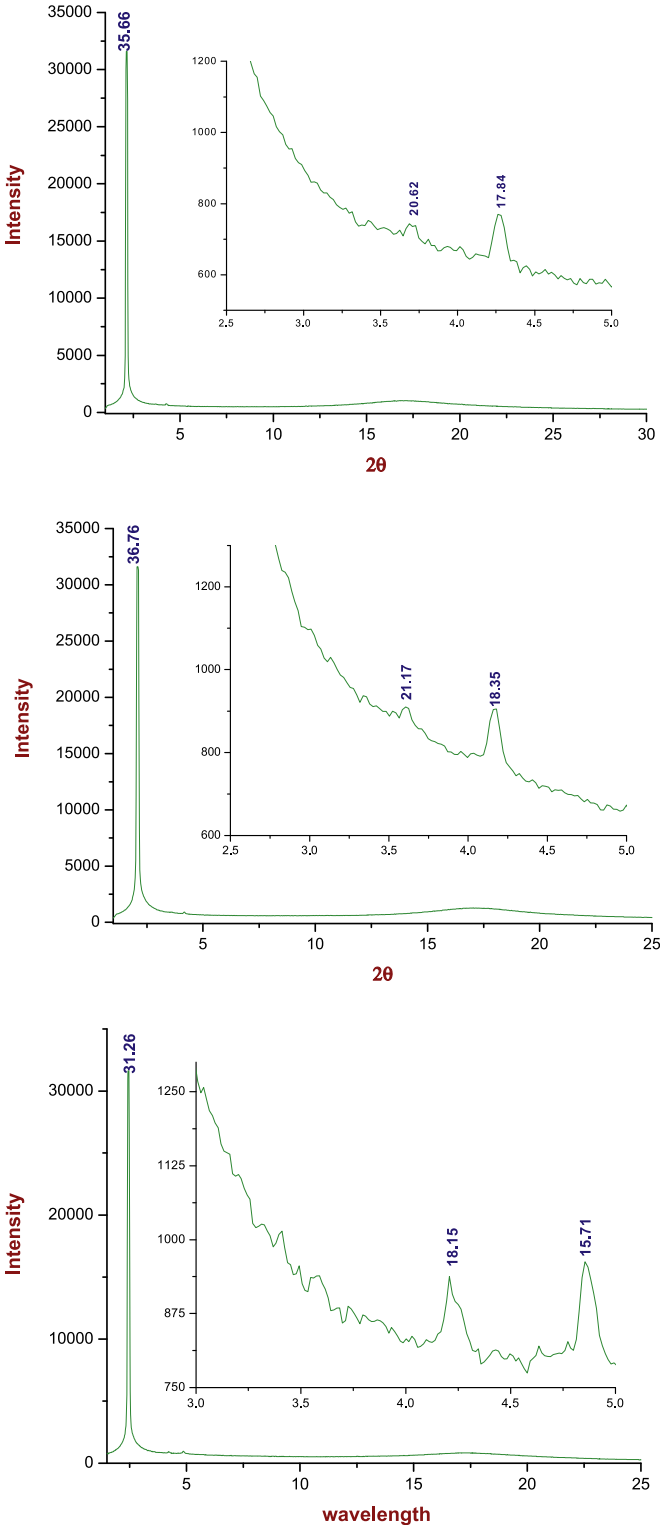


Fig. 4. The powder X-ray diffraction plots of compound **2e** at 90 °C (top), **2f** at 65.0 °C, and **1b** at 41.0 °C (bottom).

chains were probably not or slightly interdigitated both in the crystal phase and the mesophase when lower carbon considered.

2.5. Packing study of compounds 2b and 1b in hexagonal columnar phases

A simple model[10a,13] often used to calculate the number of molecules within a portion of height h has been developed, and this model has been able to correlate the possible molecular arrangement in columnar phases. In order to get more insight the molecular organizations in columnar phases, two important parameters, N_{cel} and R_{ar} were calculated from XRD diffraction data combined with single crystallographic data for compounds **2b** and **1b**. In this approach, a columnar structure is often considered to be constructed by columnar cross section (S_{col}) and the stacking periodicity along the columns (h, portion of height), according to $V_{cell}=hS_{col}=N_{cell}V_{mol}$. V_{cell} is the volume of the repeat unit (per cell), and V_{mol} is the molecular volume of one molecule. N_{cell} is the number of molecules within a column. S_{col} can be calculated from lattice parameters of X-ray diffraction. In addition, V_{mol} is composed by two components, the rigid part V_{ar} and the flexible chains, V_{ch} by the equation, $V_{mol}=V_{ar}+V_{ch}$. Another parameter to be considered is R_{ar}, defined as the diameter of the aromatic or hard columnar part, which can be calculated by $R_{ar}=(4S_{ar}/\pi)^{1/2}$. By use of the theory approach, the N_{cell} and R_{ar} parameter for two similar compounds **2b** and **1b** were obtained. An N_{cell} for compound **1b** at 70 °C and **2b** at 41 °C is 4.74 Å and 4.34 Å, whereas a R_{ar} for compound **1b** and **2b** is 17.77 Å and 16.98 Å, respectively. These two R_{ar} values were approximately half of the 38.01 Å as molecular length of **2a**. On the other hand, an average number of 4–5 molecules for **1b** and **2b** were packed within a height of 9.0 Å in the columnar phases. A distance ranged ca. 3.2–3.5 Å between the molecules within a column was often observed in columnar phases. However, compounds **1b** and **2b** were not perfectly round molecules, but triangular-shaped molecules. Therefore, a more disc-like correlated structure constructed by two molecules lying roughly side-by-side was then generated within the column. The possible molecular arrangement in columnar phases was then proposed in Fig. 5.

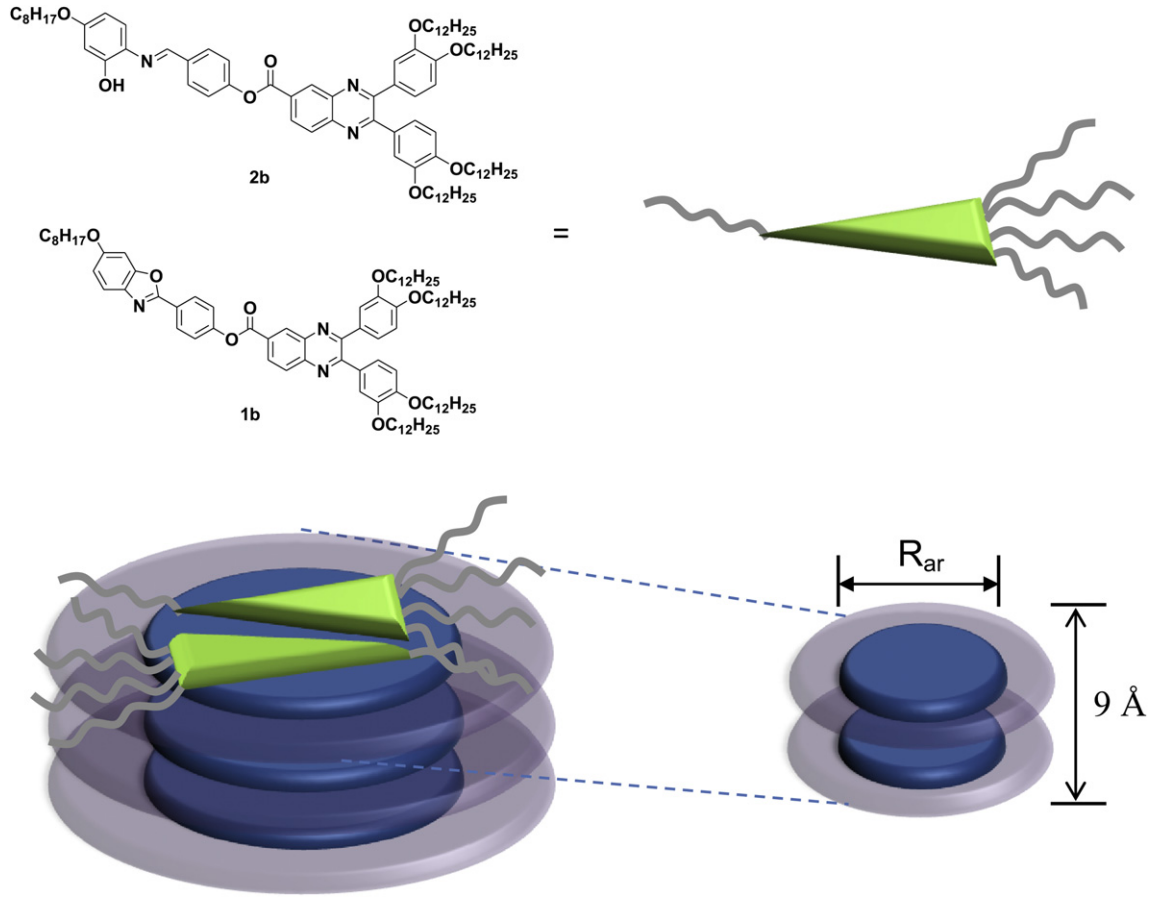


Fig. 5. A schematic representation of molecular organization in columnar phase for compounds **2b** and **1b**. Two tapered-shaped molecules lying side-by-side to generate a more disc correlated molecule was packed within a column. In a typical calculation[10a,13a] a value of 9.0 Å ($2h$=9.0 Å) has been assumed for most discotic molecules corresponding to the board signal seen in the XRD diffraction patterns.

2.6. Optical properties

The UV–vis absorption and PL spectra of the compounds **1**–**4** measured in $CHCl_3$ solution at room temperature are presented in Fig. 6. The λ_{max} peaks of UV–vis absorption and PL spectra were listed in Table 4. The absorption λ_{max} peaks occurred at ca. 379–397 nm, which were attributed to a π–π^* transition arising from quinoxalines. For compounds **1e** there appeared a strong absorption peak occurred at ~316 nm, which was attributed to benzoxazole ring. The λ_{max} peaks of UV–vis absorption and PL spectra of benzoxazole derivatives often occurred at 313–319 nm and 348–381 nm.[6] Whereas, the conjugation linked by two heterocyclic rings of quinoxaline and benzoxazole was interrupted by the connecting ester spacer. The PL spectra of all compounds showed one intense peak occurred at λ_{max}=522–525 nm, and this photoluminescent emission originated from heterocyclic quinoxaline.

Incorporation of a benzoxazole moiety to the quinoxaline would not shift their λ_{max}. An apparent red shift was often observed when an electron-donating group[1a], such as triphenylamine was incorporated. A relatively lower quantum yield ranged in 0.16–0.26 is obtained and the lower yields might be due to the effect of the lone pair on the nitrogen atom. The PL data of compounds **1e** and **2e** measured as a thin film at room temperature were also performed. The λ_{max} for compound **1e** and **2e** are 522 and 524 nm, which were slightly blue-shifted by 20 nm and 19 nm, respectively (Table 4).

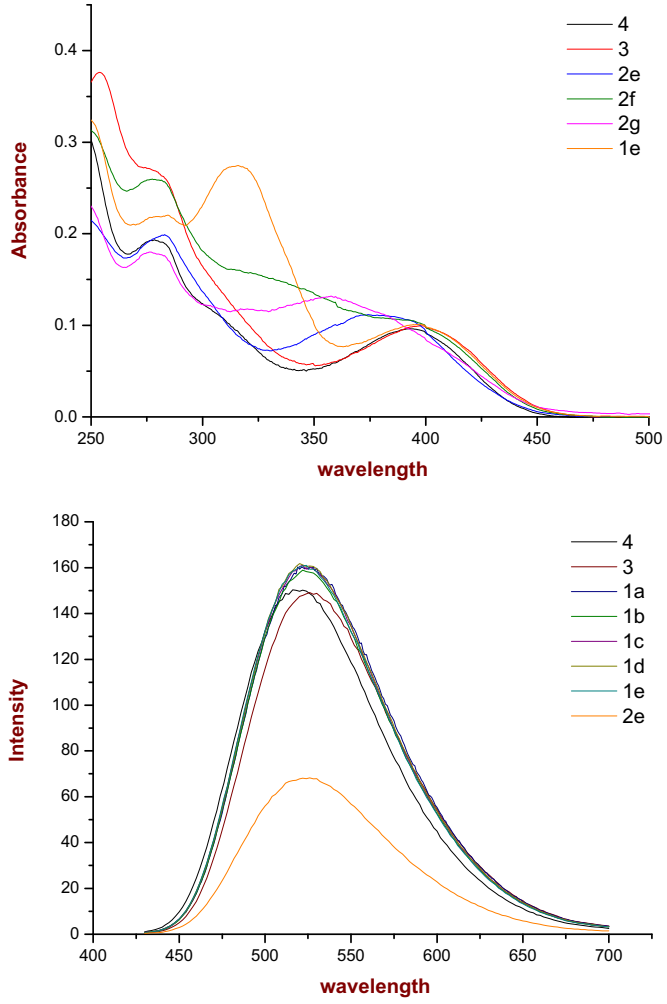


Fig. 6. Absorption (top) and fluorescent spectra (bottom) of the compounds **1**–**4**.

Table 4
Absorption and emission data[a] of compounds **1**–**4**

Compds	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Φ_f
4 (n=12)	395	522	0.26
3 (n=12)	397	525	0.22
2e	379	524 (505)[b]	0.16
1a	397	522	0.24
1b	397	522	0.26
1c	397	522	0.26
1d	397	522	0.26
1e	397	522 (502)[b]	0.26

[a] Measured in $CHCl_3$ at rt.
[b] Measured as a thin film at rt.

3. Conclusions

A series of quinoxaline-based derivatives **1** and **2** were prepared, and their mesomorphic and optical properties studied. They exhibited hexagonal columnar phases, identified by DSC, POM, and XRD. Packing studies indicated that two molecules lay side-by-side to generate a more disc-like correlated structure in the columnar phases. These materials are potentially excellent candidates for electronic devices.

4. Experimental section

4.1. General

All chemicals and solvents were reagent grade from Aldrich Chemical Co., and all solvents were dried by standard techniques. ^1H and ^{13}C NMR spectra were measured on a Bruker DRS-200. DSC thermographs were carried out on a Mettler DSC 822 and calibrated with a pure indium sample. All phase transitions are determined by a scan rate of 10.0 °C/min. Optical polarized microscopy was carried out on Zeiss Axioplan 2 equipped with a hot stage system of Mettler FP90/FP82HT. The UV–vis absorption and fluorescence spectra were obtained using a Jasco V-530 and Hitachi F-4500 spectrometer. All spectra were measured in $CHCl_3$ at room temperature, and the excitation wavelength of the fluorescent spectra was 397 nm. Elemental analyses were performed on a Heraeus CHN–O–Rapid elemental analyzer, and their mass spectra were also measured. The powder diffraction data were collected from the Wiggler-A beamline of the National Synchrotron Radiation Research Center (NSRRC) with the wavelength of 1.3263 Å. Diffraction patterns were recorded in $\theta/2\theta$ geometry with step scans normally 0.02° in 2θ=1~10° step^{-1} s^{-1} and 0.05° in 2θ=10–5° step^{-1} s^{-1} and a gas flow heater was used to control the temperature. The powder samples were charged in Lindemann capillary tubes from Charles Supper Co. with an inner diameter of 1.0 mm. The compounds of 1,2-dialkoxy benzenes, 3-alkoxyphenols, 4-alkoxy-2-nitrophenols, and 4-alkoxy-3-aminophenols were followed by literatures' procedures.[6]

4.1.1. 3-Dodeclyoxyphenol (n=12). White solid; yield 42%. ^1H NMR ($CDCl_3$): 0.86 (t, J=6.7 Hz, $-CH_3$, 3H), 1.17–1.45 (m, $-CH_2$, 18H), 1.67–1.81 (m, $-CH_2$, 2H), 3.90 (t, J=6.6 Hz, $-OCH_2$, 2H), 6.36–6.39 (d, J=6.6 Hz, –ArH, 2H), 6.49 (s, –ArH, 1H), 7.10 (t, J=8.4 Hz, –ArH, 1H). ^{13}C NMR ($CDCl_3$): 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.

4.1.2. 5-Dodecyloxy-2-nitrophenol (m=12). Yellow solid; yield 42%. ^1H NMR ($CDCl_3$): 0.86 (t, J=6.7 Hz, $-CH_3$, 3H), 1.24–1.38 (m, $-CH_2$, 18H), 1.74–1.82 (m, $-CH_2$, 2H), 3.99 (t, J=6.4 Hz, $-OCH_2$, 2H), 6.45–6.48 (d, J=6.7 Hz, –ArH, 2H), 8.00 (s, –ArH, 1H), 11.03 (s, –OH, 1H). ^{13}C NMR ($CDCl_3$): 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.

4.1.3. 2-Amino-5-dodecyloxyphenol (m=12). White solid; yield 86%. ^1H NMR ($CDCl_3$): 0.86 (t, J=6.7 Hz, $-CH_3$, 3H), 1.24–1.38 (m, $-CH_2$, 18H), 1.67–1.71 (m, $-OCH_2$, 2H), 3.84 (t, J=6.5 Hz, $-OCH_2$, 2H), 6.42–6.45 (d, J=7.6 Hz, –ArH, 2H), 6.74 (s, –ArH, 1H), 11.03(s, –OH, 1H). ^{13}C NMR ($CDCl_3$): 14.10, 23.12, 28.81, 29.25, 29.26, 29.32, 29.5, 29.49, 29.61, 31.91, 72.28, 102.17, 107.60, 117.23, 125.64, 144.53, 162.17.

4.1.4. 4-Dodecyloxy-nitrobenzene. ^1H NMR ($CDCl_3$): 0.85 (t, $-CH_3$, 3H), 1.25–1.79 (m, $-CH_2$, 20H), 4.01 (t, $-OCH_2$, 2H), 6.89 (d, J=8.0 Hz, –ArH, 2H), 8.13 (d, J=8.0 Hz, –ArH, 2H). ^{13}C NMR ($CDCl_3$): 14.11, 22.69, 25.91, 28.98, 29.32, 29.35, 29.54, 29.58, 29.64, 29.65, 31.92, 68.91, 114.39, 125.87, 141.29, 164.27.

*4.1.5. 1,2-Bis(3,4-didodecyloxyhenyl)-1,2-ethanedione (**5**, m=12).* The solution of 1, 2-didodecyloxybenzene (3.2 g, 7.18 mmol) dissolved in 30 mL carbon disulfide was added aluminum chloride (1.01 g, 7.53 mmol) under nitrogen atmosphere. The solution was vigorously stirred for a minute and the oxalyl chloride (0.35 mL,

3.95 mmol) dissolved in 20 mL of carbon disulfide was dropwise added at ice bath temperature. The solution was stirred for 8 h. The solution was concentrated under reduced pressure, and the residue was extracted with H_2O/CH_2Cl_2 (5/1). The organic layers were collected and dried over $MgSO_4$. The product isolated as milky white solids was obtained after recrystallization from CH_2Cl_2/CH_3OH. Yield 82%. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, $-CH_3$, 12H), 1.24–1.83 (m, $-CH_2$, 80H), 4.03 (t, CH_2, 8H), 6.85 (d, –ArH, 2H), 7.39 (d, –ArH, 2H), 7.55 (s, –ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.64, 25.87, 25.94, 28.87, 29.04, 29.28, 29.30, 31.72, 31.85, 53.37, 69.06, 69.18, 111.58, 112.28, 126.05, 126.16, 149.25, 154.94, 193.73.

*4.1.6. 2,3-Bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid (**4**, m=12).* The solution of 1,2-bis(3,4-didodecyloxyphenyl)-1,2-ethanedione (3.0 g, 3.17 mmol) was dissolved in 30 mL of absolute ethanol and 50 mL of dried THF under nitrogen atmosphere. The solution was added 0.5 mL of glacial acetic acid and 3,4-diaminobenzoic acid (0.579 g, 3.80 mmol), and then refluxed for 12 h. The solution was concentrated to give a brown solid, which was purified by column chromatography using hexane/ethyl acetate (1/1) as eluent. The product isolated as light yellow solids was obtained after recrystallization from acetone. Yield 90%. ^{1}H NMR ($CDCl_3$): δ 0.83–0.89 (m, $-CH_3$, 12H), 1.24–1.84 (m, $-CH_2$, 80H), 3.82 (t, J=4.6 Hz, $-OCH_2$, 4H), 3.99 (t, J=6.5 Hz, $-OCH_2$, 4H), 6.83 (d, J=8.3 Hz, –ArH, 2H), 7.10–7.16(m, –ArH, 4H), 8.17 (d, J=8.7 Hz, –ArH, 1H), 8.34 (dd, J=1.6, 8.8 Hz, –ArH, 1H), 8.94 (d, J=1.5 Hz, –ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.67, 26.01, 29.12, 29.19, 29.37, 29.42, 29.66, 31.92, 69.17, 113.04, 115.24, 122.26, 130.00, 131.11, 131.17, 132.64, 148.73, 150.17, 150.33, 154.29, 155.11, 170.99. IR (neat): 2953 (C–H), 2924 (C–H), 2870 (C–H), 2854 (C–H), 2572 (O–H), 1688 (C=O), 1599 (C=N), 1582 (C=N).

*4.1.7. 2,3-Bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-formyl phenyl ester (**3**, m=12).* Under nitrogen atmosphere the mixture of 2,3-bis-(3,4-bis-didodecyloxyphenyl)-quinoxaline-6-carboxylic acid **4** (2.50 g, 2.39 mmol) and 4-hydroxybenzoaldyhide (0.35 g, 2.87 mmol) dissolved in 50 mL of $CHCl_3$ was added 4-dimethylaminopyridine (0.38 g, 3.10 mmol) at ice bath temperature. The solution was stirred for 30 min. The ice bath was removed and the solution was slowly added *N*,*N*′-dicyclohexylcarbodiimide (0.64 g, 3.10 mmol). The solution was stirred for 12 h at room temperature. The solids were filtered off, and the solution was concentrated as light brown solids. The product isolated as yellow was obtained after recrystallization twice from acetone. Yield 71%. ^{1}H NMR ($CDCl_3$): δ 0.82–0.88 (m, $-CH_3$, 12H), 1.25–1.82 (m, $-CH_2$, 80H), 3.82 (t, J=6.2 Hz, $-OCH_2$, 4H), 3.99 (t, J=6.4 Hz, $-OCH_2$, 4H), 6.83 (d, J=8.3 Hz, –ArH, 2H), 7.10–7.18 (m, –ArH, 4H), 7.48(d, J=8.5 Hz, –ArH, 2H), 8.00 (d, J=8.6 Hz, –ArH, 2H), 8.21(d, J=8.8 Hz, –ArH, 1H), 8.41 (dd, J=1.9 , 8.8 Hz, –ArH, 1H), 9.02 (d, J=1.8 Hz, –ArH, 1H), 10.03 (s, –CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 14.14, 22.71, 26.44, 29.13, 29.21, 29.41, 29.70, 31.95, 69.16, 112.92, 115.19, 122.43, 122.88, 123.09, 129.12, 129.30, 129.60, 131.02, 131.10, 131.32, 132.32, 134.17, 140.07, 143.47, 148.69, 150.25, 150.43, 154.51, 155.36, 155.57, 163.83, 190.84. IR (neat): 2955 (C–H), 2920 (C–H), 2870 (C–H), 2850 (C–H), 1740 (C=O), 1700 (C=O), 1598 (C=N), 1581 (C=N).

4.1.8. 2,3-Bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-formyl-3-hydroxy phenyl ester. ^{1}H NMR ($CDCl_3$): δ 0.82–0.88 (m, $-CH_3$, 12H), 1.25–1.85 (m, $-CH_2$, 80H), 3.82 (t, J=6.4 Hz, $-OCH_2$, 4H), 3.99 (t, J=6.4 Hz, $-OCH_2$, 4H), 6.83 (d, J=8.4 Hz, –ArH, 2H), 6.96–7.01 (m, –ArH, 2H), 7.09–7.18 (m, –ArH, 4H), 7.64 (d, J=8.0, –ArH, 1H), 8.20 (d, J=8.8 Hz, –ArH, 1H), 8.39 (dd, J=2.0, 8.8 Hz, –ArH, 1H), 8.99 (d, J=1.8 Hz, –ArH, 1H), 9.90 (s, –CHO, 1H), 11.27(s, –OH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.07, 22.65, 25.99, 29.10, 29.16, 29.35, 29.39, 29.66, 31.89, 69.16, 110.75, 112.99, 113.84, 115.21, 118.78,122.86, 123.06, 129.09, 129.18, 129.58, 130.99, 131.09, 132.70, 136.01, 140.02, 148.69, 150.23, 150.42, 154.47, 155.34, 157.45, 163.18, 163.48, 195.44. IR (neat): 2954 (C–H), 2920 (C–H), 2871 (C–H), 2850 (C–H), 1744 (C=O), 1659 (C=O), 1621(C=N), 1600 (C=N), 1583 (C=N).

*4.1.9. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-dodecyloxy-2-hydroxyphenylimino)methyl]phenyl ester **2e**.* The mixture of 2,3-bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-formyl phenyl ester (0.30 g, 0.26 mmol) and 2-amino-5-dodecyloxyphenol (0.08 g, 0.28 mmol) was refluxed in 20 mL of absolute ethanol for 3 h. The solution was cooled and the yellow solids were collected. The products isolated as bright yellow solids were obtained after recrystallization from THF. Yield 89%. ^{1}H NMR ($CDCl_3$): δ 0.84–0.88 (m, $-CH_3$, 15H), 1.25–1.82 (m, $-CH_2$, 100H), 3.81–3.83 (m, $-OCH_2$, 4H), 3.93–4.00 (m, $-OCH_2$, 6H), 6.46 (dd, J=2.8 , 8.7 Hz, –ArH, 1H), 6.57 (d, J=2.6 Hz, –ArH, 1H), 6.83 (d, J=8.2 Hz, –ArH, 2H), 7.09–7.15 (m, –ArH, 4H), 7.29 (d, J=8.9 Hz, –ArH, 1H), 7.40 (d, J=8.6, –ArH, 2H), 7.97 (d, J=8.6, –ArH, 2H), 8.21 (d, J=8.7 Hz, –ArH, 1H), 8.42 (dd, J=1.8 , 8.7 Hz, –ArH, 1H), 8.65 (s, –CHN, 1H), 9.03 (d, J=1.6 Hz, –ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.02, 29.14, 29.20, 29.34, 29.38, 29.42, 29.45, 29.57, 29.59, 29.64, 29.66, 29.69, 29.74, 31.92, 68.29, 69.17, 69.22, 100.52, 107.19, 113.04, 113.08, 115.20, 115.28, 116.20, 122.11, 122.90, 123.09, 128.24, 129.20, 129.51, 129.58, 129.72, 131.12, 131.18, 132.60, 134.16, 140.12, 143.40, 148.75, 150.25, 150.43, 152.22, 152.98, 153.85, 154.43, 160.42, 164.21. IR (neat): 3445 (O–H), 2953 (C–H), 2921 (C–H), 2869 (C–H), 2851 (C–H), 1735 (C=O), 1624 (C=N), 1601 (C=N), 1582 (C=N). Anal. Calcd for $C_{94}H_{143}N_3O_8$: C, 78.23; H, 9.99. Found: C, 78.13; H, 10.06. MS (FAB, m/z): 1444.0 (M^+).

*4.1.10. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-butoxy-2-hydroxy phenylimino)methyl]phenyl ester **2a**.* ^{1}H NMR ($CDCl_3$): δ 0.86–1.00 (m, $-CH_3$, 15H), 1.25–1.81 (m, $-CH_2$, 36H), 3.83 (t, J=6.6 Hz, $-OCH_2$, 4H), 3.91–4.04 (m, $-OCH_2$, 6H), 6.46 (d, J=2.6 , 8.8 Hz, –ArH, 1H), 6.56 (d, J=2.6 Hz, –ArH, 1H), 6.84 (d, J=8.4 Hz, –ArH, 2H), 7.09–7.18 (m, –ArH, 4H), 7.29 (d, J=9.0 Hz, –ArH, 1H), 7.40 (d, J=8.6 Hz, –ArH, 2H), 7.96 (d, J=8.6 Hz, –ArH, 2H), 8.21 (d, J=8.8 Hz, –ArH, 1H), 8.43 (dd, J=1.9 , 8.8 Hz, –ArH, 1H), 8.64 (s, –CHN, 1H), 9.03 (d, J=1.6 Hz, –ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 13.78, 13.85, 14.11, 19.15, 19.19, 22.67, 26.00, 29.18, 29.33, 29.37, 29.58, 29.62, 31.07, 31.18, 31.90, 68.27, 68.78, 68.83, 100.48, 107.17, 112.98, 115.20, 116.20, 122.10, 123.05, 128.22, 129.50, 129.58, 129.70, 131.07, 131.14, 132.58, 134.13, 140.10, 143.37, 148.70, 150.21, 150.39, 152.20, 152.95, 153.83, 154.40, 155.23, 160.39, 164.20. Anal. Calcd for $C_{62}H_{79}N_3O_8$: C, 74.89; H, 8.01. Found: C, 74.78; H, 8.11. MS (FAB, m/z): 995.6 (M^+).

*4.1.11. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-butoxy-2-hydroxy phenylimino)methyl]phenyl ester **2b**.* ^{1}H NMR ($CDCl_3$): δ 0.83–0.89 (m, $-CH_3$, 15H), 1.25–1.85 (m, $-CH_2$, 36H), 3.83 (t, J=6.7 Hz, $-OCH_2$, 4H), 3.91–4.03 (m, $-OCH_2$, 6H), 6.46 (dd, J=2.7 , 8.8 Hz, –ArH, 1H), 6.56 (d, J=2.6 Hz, –ArH, 1H), 6.83 (d, J=8.2 Hz, –ArH, 2H), 7.10–7.18 (m, –ArH, 4H), 7.29 (d, J=9.0 Hz, –ArH, 1H), 7.40 (d, J=8.6 Hz, –ArH, 2H), 7.97 (d, J=8.7 Hz, –ArH, 2H), 8.21 (d, J=8.7 Hz, –ArH, 1H), 8.43 (dd, J=1.9 , 8.8 Hz, –ArH, 1H), 8.64 (s, –CHN, 1H), 9.03 (d, J=1.8 Hz, –ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 25.99, 29.11, 29.17, 29.26, 29.34, 29.57, 29.61, 31.81, 31.89, 68.25, 69.17, 100.49, 107.15, 112.96, 115.13, 116.19, 122.08, 122.89, 123.07, 128.20, 129.56, 129.68, 131.08, 131.14, 132.58, 134.12, 140.08, 143.37, 148.71, 150.21, 150.38, 152.18, 152.94, 153.83, 154.41, 155.23, 160.38, 164.17. Anal. Calcd for $C_{78}H_{111}N_3O_8$: C, 76.87; H, 9.18. Found: C, 76.89; H, 9.26. MS (FAB, m/z): 1219.9 (M^+).

*4.1.12. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-butoxy-2-hydroxy phenylimino)methyl]phenyl ester **2c**.* ^{1}H NMR ($CDCl_3$): δ 0.83–1.00 (m, $-CH_3$, 15H), 1.25–1.82 (m, $-CH_2$, 84H), 3.82 (t, J=6.6 Hz, $-OCH_2$, 4H), 3.92–4.02 (m, $-OCH_2$, 6H),

6.46(d, *J*=2.6 , 8.8 Hz, −ArH, 1H), 6.57 (d, *J*=2.6 Hz, −ArH, 1H), 6.83 (d, *J*=8.3 Hz, −ArH, 2H), 7.10–7.18 (m, −ArH, 4H), 7.29 (d, *J*=8.9 Hz, −ArH, 1H), 7.40 (d, *J*=8.6 Hz, −ArH, 2H), 7.97 (d, *J*=8.6 Hz, −ArH, 2H), 8.21 (d, *J*=8.7 Hz, −ArH, 1H), 8.43 (dd, *J*=1.8 , 8.8 Hz, −ArH, 1H), 8.64 (s, −CHN, 1H), 9.03 (d, *J*=1.7 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 13.81, 14.08, 19.21, 22.66, 26.00, 29.11, 29.19, 29.36, 29.41, 29.67, 31.22, 31.91, 67.92, 69.18, 100.49, 107.14, 113.00, 115.18, 116.19, 122.08, 122.88, 123.06, 128.22, 129.19, 129.56, 129.69, 131.09, 131.16, 132.58, 134.12, 140.09, 143.37, 148.72, 150.22, 150.40, 152.19, 152.95, 153.83, 154.40, 155.23, 160.38, 164.17. Anal. Calcd for $C_{86}H_{127}NO_8$: C, 77.61; H, 9.62. Found: C, 77.40; H, 9.33. MS (FAB, *m*/*z*): 1331.9 (M^+).

4.1.13. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-octloxy-2-hydroxy phenylimino)methyl]phenyl ester ***2d***. ^{1}H NMR ($CDCl_3$): δ 0.83–0.88 (m, −CH_3, 15H), 1.25–1.82 (m, −CH_2, 92H), 3.82 (t, *J*=6.2 Hz, −OCH_2, 4H), 3.91–4.03 (m, −OCH_2, 6H), 6.46 (d, *J*=2.6 , 9.0 Hz, −ArH, 1H), 6.57 (d, *J*=2.5 Hz, −ArH, 1H), 6.83 (d, *J*=8.3 Hz, −ArH, 2H), 7.10–7.18 (m, −ArH, 4H), 7.29 (d, *J*=8.9 Hz, −ArH, 1H), 7.40 (d, *J*=8.5 Hz, −ArH, 2H), 7.97 (d, *J*=8.6 Hz, −ArH, 2H), 8.21 (d, *J*=8.8, −ArH, 1H), 8.40 (dd, *J*=1.7 , 8.8 Hz, −ArH, 1H), 8.64 (s, −CHN, 1H), 9.03 (d, *J*=1.7 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.67, 26.02, 29.13, 29.21, 29.36, 29.42, 29.66, 31.80, 31.97, 68.28, 69.20, 100.51, 107.17, 113.05, 115.19, 116.20, 122.10, 122.90, 128.23, 129.20, 129.58, 129.71, 131.11, 131.18, 132.60, 134.14, 140.11, 143.39, 148.76, 150.24, 150.42, 152.21, 152.97, 153.84, 154.42, 155.25, 160.40, 164.19. Anal. Calcd for $C_{90}H_{135}N_3O_8$: C, 77.93; H, 9.81. Found: C, 77.79; H, 9.90. MS (FAB, *m*/*z*): 1388.0 (M^+).

4.1.14. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-dodecyloxyphenyl imino)methyl]phenyl ester ***2f***. Yellow solids; yield 80%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.87 (m, −CH_3, 15H), 1.25–1.82 (m, −CH_2, 100H), 3.81–3.83 (m, −OCH_2, 4H), 3.95–4.00 (m, −OCH_2, 6H), 6.82 (d, *J*=1.5 Hz, −ArH, 2H), 6.40 (d, *J*=1.5 Hz, −ArH, 1H) 7.10–7.14 (m, −ArH, 4H), 7.22 (s, −ArH, 2H), 7.39 (d, *J*=8.5 Hz, −ArH, 2H), 7.98 (d, *J*=8.5 Hz, −ArH, 2H), 8.21 (d, *J*=8.7 Hz, −ArH, 1H), 8.42 (dd, *J*=1.4 , 8.7 Hz, −ArH, 1H), 8.49 (s, −CHN, 1H), 9.02 (d, *J*=1.5 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 26.02, 29.14, 29.21, 29.36, 29.40, 29.42, 29.45, 29.57, 29.59, 29.63, 29.66, 29.68, 29.74, 31.91, 68.30, 69.17, 69.22, 113.07, 115.01, 115.23, 115.31, 121.97, 122.18, 122.90, 123.08, 129.48, 129.80, 131.16, 132.58, 134.44, 140.12, 143.38, 144.57, 148.75, 148.78, 150.25, 150.42, 152.93, 154.39, 156.79, 158.00, 164.20. IR (neat): 2956 (C–H), 2920 (C–H), 2871 (C–H), 2851 (C–H), 1735 (C=O), 1624 (C=N), 1600 (C=N), 1581 (C=N). Anal. Calcd for $C_{94}H_{143}N_3O_7$: C, 79.1; H, 10.10. Found: C, 79.43; H, 10.11. MS (FAB, *m*/*z*): 1427.9 (M^+).

4.1.15. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-[(4-dodecyloxyphenyl imino)methyl]-3-hydroxyphenyl ester ***2g***. ^{1}H NMR ($CDCl_3$) δ 0.86 (m, −CH_3, 15H), 1.25–1.81 (m, −CH_2, 100H), 3.80–3.84 (m, −OCH_2, 4H), 3.97–3.99 (m, −OCH_2, 6H), 6.82–6.95 (m, −ArH, 6H), 7.10–7.15 (m, −ArH, 4H), 7.26(d, *J*=8.4 Hz, −ArH, 2H), 7.42 (d, *J*=8.3 Hz, −ArH, 1H), 8.20 (d, *J*=8.6 Hz, −ArH, 1H), 8.41 (d, *J*=8.6 Hz, −ArH, 1H), 8.62 (s, −CHN, 1H), 9.00 (s, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 29.13, 29.20, 29.37, 29.42, 29.45, 29.56, 29.60, 29.64, 29.66, 29.69, 29.74, 31.91, 68.36, 69.17, 69.21, 110.40, 112.63, 113.06, 113.09, 115.22, 115.29, 117.60, 122.25, 122.90, 123.07, 129.23, 129.45, 129.79, 131.16, 131.21, 132.59, 132.83, 140.12, 140.79, 143.37, 158.75, 148.77, 150.22, 150.40, 154.14, 154.37, 155.20, 158.56, 159.27, 162.50, 164.01. IR (neat): 2955 (C–H), 2919 (C–H), 2870 (C–H), 2851(C–H), 1736 (C=O), 1617 (C=N), 1598 (C=N), 1578 (C=N). Anal. Calcd for $C_{94}H_{143}N_3O_8$: C, 78.23; H, 9.99. Found: C, 78.17; H, 10.10. MS (FAB, *m*/*z*): 1444.0 (M^+).

4.1.16. 2,3-Bis(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-(6-dodecyloxy benzoxazol-2-yl)phenyl ester ***1e***. The solution of 2,3-bis-(3,4-bis-didodecyloxyphenyl)-quinoxaline-6-carboxylic acid 4-[(4-dodecyloxy-2-hydroxyphenylimino)methyl]phenyl ester (0.30 g, 0.21 mmol) dissolved in 10 mL of $CHCl_3$ was added Pb$(OAc)_4$ (0.11 g, 0.25 mmol) under nitrogen atmosphere. The solution was gently refluxed for 2 h. The solution was extracted twice with 100 mL of CH_2Cl_2/H_2O (1/4) each, and the organic layers were combined and dried over $MgSO_4$. The solution was concentrated to give light brown solids. The product isolated as light yellow solids was obtained after recrystallization from acetone. Yield 75%. ^{1}H NMR ($CDCl_3$): δ 0.85–0.88 (m, −CH_3, 15H), 1.25–1.84 (m, −CH_2, 100H), 3.81–3.84 (m, −OCH_2, 4H), 3.98–4.02 (m, −OCH_2, 6H), 6.83 (d, *J*=8.3 Hz, −ArH, 2H), 6.95 (dd, *J*=2.3 , 8.8 Hz, −ArH, 1H), 7.09–7.17 (m, −ArH, 5H), 7.45 (d, *J*=8.5 Hz, −ArH, 2H), 7.62 (d, *J*=8.7 Hz, −ArH, 1H), 8.21 (d, *J*=8.7 Hz, −ArH, 1H), 8.29 (d, *J*=8.5 Hz, −ArH, 2H), 8.41 (dd, *J*=1.9 , 8.8 Hz, −ArH, 1H), 9.02 (d, *J*=1.4 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.02, 26.04, 29.14, 29.22, 29.36, 29.38, 29.42, 29.45, 29.59, 29.64, 29.66, 29.69, 29.74, 31.92, 68.90, 69.18, 69.23, 96.08, 113.07, 113.10, 113.50, 115.24, 115.32, 119.97, 122.21, 122.91, 123.09, 125.31, 128.61, 129.18, 129.53, 129.65, 131.14, 131.20, 132.64, 140.13, 143.40, 148.77, 148.79, 150.24, 150.41, 151.71, 153.04, 154.43, 155.26, 157.92, 161.37, 164.14. Anal. Calcd for $C_{94}H_{141}N_3O_8$: C, 78.34; H, 9.86. Found: C, 78.12; H, 9.88. MS (FAB, *m*/*z*): 1442.0 (M^+).

4.1.17. 2,3-Bis(3,4-dibutoxyphenyl)quinoxaline-6-carboxylic acid 4-(6-dodecyloxy benzoxazol-2-yl)phenyl ester ***1a***. ^{1}H NMR ($CDCl_3$): δ 0.84–1.00 (m, −CH_3, 15H), 1.25–1.84 (m, −CH_2, 36H), 3.83 (t, *J*=5.6 Hz, −OCH_2, 4H), 3.97–4.04 (m, −OCH_2, 6H), 6.84 (d, *J*=8.4 Hz, −ArH, 2H), 6.94 (dd, *J*=2.1 , 8.8 Hz, −ArH, 1H), 7.09–7.17 (m, −ArH, 5H), 7.45 (d, *J*=8.8 Hz, −ArH, 2H), 7.62(d, *J*=8.7, −ArH, 1H), 8.21 (d, *J*=8.8 Hz, −ArH, 1H), 8.28 (d, *J*=8.8 Hz, −ArH, 2H), 8.42 (dd, *J*=1.9 , 8.8 Hz, −ArH, 1H), 9.03 (d, *J*=1.7 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 13.77, 13.84, 14.09, 19.15, 19.19, 22.66, 26.04, 29.21, 29.32, 29.57, 29.61, 31.08, 31.19, 31.89, 68.80, 68.84, 96.05, 113.01, 113.43, 115.17, 119.95, 122.20, 122.87, 123.05, 125.29, 128.59, 129.52, 129.63, 131.09, 131.15, 132.62, 135.69, 140.11, 143.41, 148.72, 150.23, 150.41, 151.70, 153.00, 154.42, 155.20, 157.90, 161.35, 164.14. Anal. Calcd for $C_{62}H_{77}N_3O_8$: C, 75.04; H, 7.82. Found: C, 75.05; H, 7.94. MS (FAB, *m*/*z*): 993.3 (M^+).

4.1.18. 2,3-Bis-(3,4-dioctloxyphenyl)quinoxaline-6-carboxylic acid 4-(6-dodecyloxy benzoxazol-2-yl)phenyl ester ***1b***. ^{1}H NMR ($CDCl_3$): δ 0.84–0.87 (m, −CH_3, 15H), 1.26–1.85 (m, −CH_2, 68H), 3.83 (t, *J*=6.3 Hz, −OCH_2, 4H), 3.97–4.02 (m, −OCH_2, 6H), 6.83 (d, *J*=8.2 Hz, −ArH, 2H), 6.94 (dd, *J*=2.1 , 8.8 Hz, −ArH, 1H) 7.11–7.18 (m, −ArH, 5H), 7.45 (d, *J*=8.7, −ArH, 2H), 7.62 (d, *J*=8.7 Hz, −ArH, 1H), 8.21(d, *J*=8.8, −ArH, 1H), 8.28 (d, *J*=8.6 Hz, −ArH, 2H) 8.42 (dd, *J*=1.7 , 8.8 Hz, −ArH, 1H), 9.02 (d, *J*=1.6 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.63, 25.97, 29.10, 29.16, 29.23, 29.32 29.35, 29.55, 31.56, 31.78, 31.87, 68.81, 69.14, 95.99, 112.95, 113.43, 115.13, 119.91, 122.16, 122.87, 123.05, 125.23, 128.54, 129.47, 129.58, 131.06, 131.12, 132.58, 135.64, 140.06, 143.36, 148.68, 150.20, 150.37, 151.66, 152.99, 154.37, 155.20, 157.86, 161.31, 164.07. Anal. Calcd for $C_{78}H_{109}N_3O_8$: C, 77.00; H, 9.03. Found: C, 77.02; H, 9.31. MS (FAB, *m*/*z*): 1217.8 (M^+).

4.1.19. 2,3-Bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-(6-butoxy benzoxazol-2-yl)phenyl ester ***1c***. ^{1}H NMR ($CDCl_3$): δ 0.86–1.02 (m, −CH_3, 15H), 1.25–1.85 (m, −CH_2, 84H), 3.82 (t, *J*=6.5 Hz, −OCH_2, 4H), 3.96–4.05 (m, −OCH_2, 6H), 6.83 (d, *J*=8.3 Hz, −ArH, 2H), 6.95 (dd, *J*=2.3, 8.8 Hz, −ArH, 1H), 7.10–7.18 (m, −ArH, 5H), 7.45 (d, *J*=8.7 Hz, −ArH, 2H), 7.62 (d, *J*=8.7 Hz, −ArH, 1H), 8.21 (d, *J*=8.7 Hz, −ArH, 1H), 8.29 (d, *J*=8.7 Hz, −ArH, 2H), 8.41 (dd, *J*=1.8 , 8.8 Hz, −ArH, 1H), 9.03 (d, *J*=1.6 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.65, 25.99, 29.10, 29.17, 29.35, 29.39 29.42, 29.64, 31.89, 68.48, 69.10, 95.98, 112.96, 113.43, 115.21, 119.91, 122.16, 122.90, 123.05, 125.31, 128.56, 129.13, 129.58, 131.06, 131.12, 132.58,

135.66, 140.06, 143.36, 148.68, 150.20, 150.37, 151.66, 152.97, 154.37, 155.20, 157.66, 161.31, 164.06. Anal. Calcd for $C_{86}H_{125}N_3O_8$: C, 77.73; H, 9.48. Found: C, 77.83; H, 9.70. MS (FAB, *m*/*z*): 1329.9 (M^+).

4.1.20. 2,3-Bis-(3,4-didodecyloxyphenyl)quinoxaline-6-carboxylic acid 4-(6-octloxy benzoxazol-2-yl)phenyl ester ***1d***. ^{1}H NMR ($CDCl_3$): δ 0.86–0.88 (m, $-CH_3$, 15H), 1.25–1.85 (m, $-CH_2$, 92H), 3.82 (t, *J*=6.5 Hz, $-OCH_2$, 4H), 3.96–4.03 (m, $-OCH_2$, 6H), 6.83 (d, *J*=8.3 Hz, −ArH, 2H), 6.95 (dd, *J*=2.3 , 8.8 Hz, −ArH, 1H) 7.10–7.19 (m, −ArH, 5H), 7.45 (d, *J*=8.7 Hz, −ArH, 2H), 7.62 (d, *J*=8.8, −ArH, 1H), 8.21 (d, *J*=8.8 Hz, −ArH, 1H), 8.28 (d, *J*=8.7 Hz, −ArH, 2H), 8.41 (dd, *J*=1.9 , 8.8 Hz, −ArH, 1H), 9.03 (d, *J*=1.4 Hz, −ArH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.67, 26.02, 29.13, 29.22, 29.36, 29.44, 29.67, 31.80, 31.91, 68.88, 69.20, 96.06, 113.03, 113.94, 115.18, 119.95, 122.90, 123.07, 125.29, 128.60, 129.18, 129.63, 131.10, 131.16, 132.63, 135.70, 140.11, 143.40, 148.74, 150.24, 150.41, 151.71, 153.02, 154.43, 155.26, 157.37, 161.37, 164.14. Anal. Calcd for $C_{90}H_{133}N_3O_8$: C, 78.05; H, 9.68. Found: C, 78.62; H, 9.79. MS (FAB, *m*/*z*): 1386.9 (M^+).x

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References and notes

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