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Symmetric mesogenic twins derived from salicylaldimines

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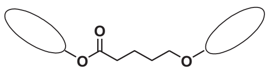
ABSTRACT

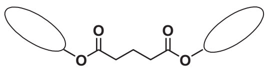
The synthesis, characterization, and mesomorphic properties of a series of symmetric dimeric twins derived from mesogenic salicylaldimines **1a**–**e** are reported. In order to understand the structure–property relations, the bridged spacer (m=5, 6, 7, 8, 9), and alkoxy chains (n=6, 8, 10, 12, 14) were systematically varied. Except for **1a**, all derivatives **1b**–**e** exhibited mesophases whose mesomorphic properties strongly depended on the spacer parity and the alkoxy chains. Dimers **1a** exhibited crystal or SmX phases. Other dimers **1b**–**e** were truly mesogenic, giving enantiotropic SmC, SmA or/and N phases. Odd–even effect was observed on phase temperatures, and nematic phases were observed for derivatives with odd spacer, and a value of d/l=0.92 (**1a**; m=5, n=8)–0.84 (**1c**; m=7, n=14) was obtained by powder X-ray diffraction data, therefore, a monolayer structure in mesophase was proposed.

1. Introduction

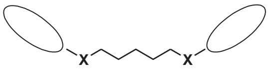
Mesogenic dimers, or so-called twins or bimesogens have attracted scientific attention since the discovery of the first example[1] reported on 1927. All these dimeric structures[2] generally contained two non-identical **Ia** (unsymmetric) or identical **Ib** (symmetric) core moieties linked or bridged by a flexible central spacer. Then a sequence of rigid mesogen-flexible spacer-rigid mesogen in a twin structure was therefore obtained. A variety of flexible spacers, such as alkylene[3] $[-(CH_2)_n-]$ **Ic**, dioxyalkylene[4] $[-O(CH_2)_nO-]$ **Id** or ester[5] $[-COO(CH_2)_nOOC-]$ **Ib** have been incorporated to obtain such twins. Interestingly, an apparent effect observed when replacing the alkyloxy chains in **Ic** by alkylsulphanyl chains in **Id** on the formation of mesophases was attributed to their molecular flexibilities[6] known as the order: R–O–<R–S–<R–CH$_2$–. Sulfur atom was also considered as more polarizable than oxygen atom. A few mesogenic examples constructed by a siloxane core[7] of varying length in the central region was also studied. Such dimers have high conformational flexibility in the central part of the molecule and also have terminal groups with high spatial anisomery. The resulting mesomorphic properties were significantly influenced by their core structures, the spacer lengths, and the linker groups as well.



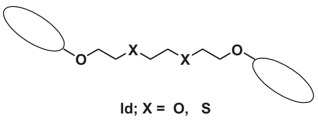
Ia



Ib



Ic; X = O, S



Id; X = O, S

An odd–even effect,[8] referred to the spacer parity-dependent mesomorphic properties was observed due to their possibly existing conformations in this type of dimeric structures. The derivatives with even spacers often possess higher phase transition temperatures than those of the derivatives with the odd spacers, which were attributed to their better structural linearity. In contrast, the molecular shapes of derivatives with odd spacers were likely less linear. However, an unusual example[9] of odd liquid crystalline dimers was found to be linear. The single crystallographic data showed that the odd dimer crystallizes adopting a molecular conformation in which the two mesogenic groups are aligned with respect to each other, as for the even dimer. Dimers were particularly interesting due to their unique thermal behavior and structural features as model compounds similar to the polymeric liquid crystals. Compared to the conventional rod-like mesogens, the transitional properties produced by dimeric mesogens are in fact modified to a much larger extent by changes in the length and parity[10] of the alkyl chains. The difference in phase behavior was mostly attributed to the

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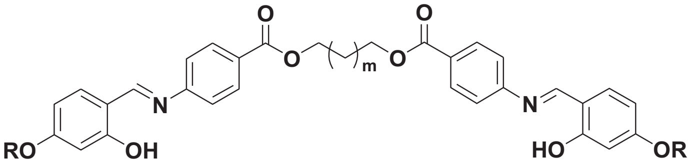
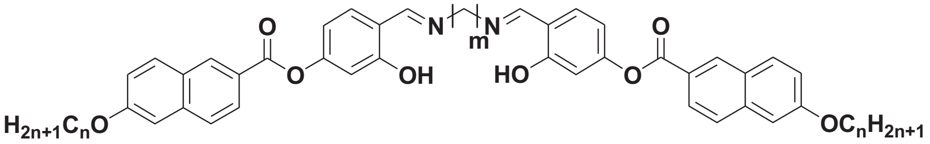
dependence of the molecular shape and/or geometry on the parity of the central spacer when considered in the all-trans conformation. In the all-trans conformations[11] the two mesogenic cores are arranged with an anti-parallel style, whereas in the all-cis conformation they are slightly inclined with a bending angle to each other. Most twin compounds formed layer smectic phases, in which smectic intercalated, monolayer, and interdigitated phases were commonly observed. Non-symmetric LC dimers usually exhibited intercalated smectic phases, whereas, the symmetric LC dimers formed monolayer smectic phases. In additions, a ferroelectric or antiferroelectric phase was reported on some chiral twins.[3a,12] Known examples of columnar twins[13] were relatively limited; a connection of two bent-core units linked with tetraethylene glycol spacer resulted in a formation of columnar phases. Furthermore, an unconventional T-shaped non-symmetric dimeric LC[14] was recently reported, in which the spacer was proposed to adopt conformations with two mesogenic units held more or less parallel.



III; m = 1, 3; R = $(CH_2)_nH$

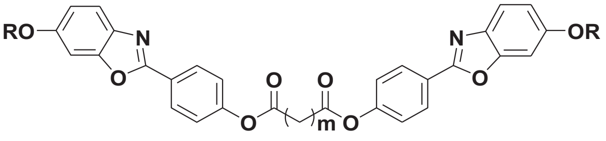


1a m = 5, n = 6, 8, 10, 12, 14
1b m = 6, n = 12
1c m = 7, n = 6, 8, 10, 12, 14
1d m = 8, n = 12
1e m = 9, n = 6, 8, 10, 12, 14

Among the reported LC dimers, examples of the rigid mesogens were known, such as Schiff bases, stilbenes, aromatics, cholesterols, and tolan moieties. Two symmetric twins incorporated with two mesogenic heterocyclic benzoxazoles **II**[15] or 1,3,4-oxadiazoles[16] were also reported. A series of dimeric twins derived from symmetric heterocyclic benzoxazoles **II** exhibiting single smectic C phase were reported by this group. The formation of SmC phases was attributed to the weak dipole force induced by donor–acceptor interaction (D→A). A monolayer conformation was proposed based on the powder XRD data. A value of entropy changes $\Delta S_{(\mathrm{SmC}\rightarrow\mathrm{I})}/R$=2.00–6.50 associated in twin system due to odd–even effects was found.

Both series of compounds **II** and **III** are considered as rod-like twin mesogens. However, known examples derived from mesogenic salicylaldimines[17] **III** were relatively rare. Intramolecular or intermolecular H-bonds induced in central core salicylaldimines might play an important role in stabilizing the mesophases. Compounds **III** are not heterocyclic and a mixed phase, as nematic, smectic A, smectic C or smectic X phase was indeed observed in compounds **III**, indication that a lateral interaction of side-by-side molecules are also important.

In this work, we describe the synthesis, characterization, and mesomorphic studies of a new series of symmetric dimers derived from naphthalene substituted salicylaldimines bridged by a methylene as spacer group. These dimeric twins exhibited interesting mesomorphic behavior. Derivatives **1a** with shorter spacers (m=5) were not mesogenic. In contrast, all other derivatives **1b**–**e** with longer spacers (m=6, 7, 8, 9) were truly mesogenic, giving nematic, smectic or smectic C phases. A monolayer conformation in the SmC phase was proposed based on XRD diffraction experiments.



II; m = 3-11; n = 6-16; R = $(CH_2)_nH$

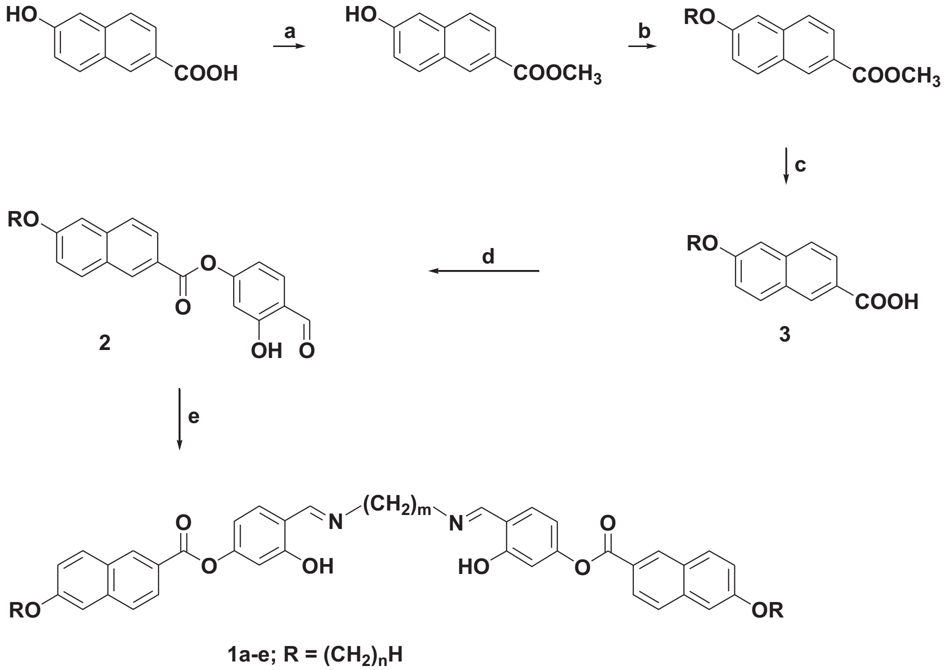
2. Results and discussion

2.1. Synthesis and characterization

The synthetic procedures used to prepare compounds **1a**–**e** in this work are given in Scheme 1. All compounds of 6-hydroxy-naphthalene-2-carboxylic acid methyl ester, 6-alkoxy-naphthalene-2-carboxylic acid methyl esters, and 6-alkoxy-naphthalene-2-carboxylic acids **3** were similarly prepared according to literature. The aldimine Schiff-base derivatives isolated as light yellow crystals were obtained by condensation reactions of naphthalene-2-carboxylic acid 4-formyl-3-hydroxyphenyl esters and alkyldiamines in refluxing absolute ethanol. The yields were ranged in 77–85%. All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. For example, the ^{1}H NMR spectroscopic data (Table 1) of compounds **1a**–**e** showed one characteristic peak at δ 8.31–8.34 ppm, assigned to imine–H (–N=CH). The purity of final compounds **1a**–**e** was also confirmed by elemental analysis.

2.2. Mesomorphic properties and thermal stability

The liquid crystalline behavior of compounds **1a**–**e** was characterized and investigated by differential scanning calorimetry and polarized optical microscope. The phase transitions and thermodynamic data are summarized in Table 2. The formation of mesophases was dependent on the length of the spacer and the terminal chains. All dimers **1a** appended with a shorter spacer of C_5-methylene exhibited crystal or/and highly ordered smectic X phases. For



Scheme 1. Reagents and conditions. (a) H2SO4 (concd), refluxed in CH3OH, 24 h, 90%; (b) RBr (1.1 equiv), K2CO3 (2.0 equiv), KI, refluxing in dried CH3COCH3, 24 h, 78–88%; (c) KOH, refluxed in C2H5OH/H2O (8/2), 24 h, 90–93%; (d) 2,4-dihydroxybenzaldehyde (1.0 equiv), DCC, DMAP, stirred in dried CH2Cl2, 24 h. 64–72%; (e) alkyldiamines (0.5 equiv), refluxing in absolute C2H5OH, 24 h, 75–92%.

Table 1
Characteristic chemical peaks[a] on ^{1}H and ^{13}C NMR spectroscopes in compounds **1a**–**e** and **2**

Functional group	–C*H*=O in **2** (*n*=12)	–C*H*=N in **1a**–**e**
Spectroscope		
^{1}H NMR	9.87–9.88	8.31–8.34
^{13}C NMR	195.50–195.52	165.06–165.38

[a] Samples with a concentration of ~1.0×10^{-3} M measured in CDCl$_3$; δ in ppm.

the dimers **1b**–**e** bridged with a longer spacer of –C$_6$–, –C$_7$–, –C$_8$–, and –C$_9$–methylene were truly liquid crystals, giving an enantiotropic SmC, SmA or/and N phase. In these dimers, the spacer has a significant influence on the thermal behavior. An odd–even effect on the melting and clearing temperatures was also observed.

For the dimer **1a** appended with the shortest spacer (*m*=5), the derivative *n*=6 was not mesogenic and all other four derivatives *n*=8, 10, 12, 14 formed highly ordered smectic X phases. The melting temperatures were ranged from 108.8–121.7 °C. The clearing temperatures were ranged from 128.9–153.7 °C, which were increased with carbon lengths. The temperature range of SmX phases is ca. ΔT_{SmX}=29.0 (*n*=8)<52.1 (*n*=10)<55.0 (*n*=12)<55.2 °C (*n*=14). A texture of mosaic domains under optical microscope was obtained when cooling from isotropic liquid (Fig. 1). The exact phase was not attempted to identify. A highly ordered phase was confirmed by variable temperature powder X-ray diffraction experiments.

On the other hands, all other derivatives **1b**–**e** formed enantiotropic phases regardless of the alkoxy chain lengths. These derivatives all exhibited nematic, smectic A, and/or smectic C phases, as expected for the rod-like molecules. Two derivatives **1b** with even spacers (*m*=6) and **1d** (*m*=8), and one derivative **1e** with odd spacer (*m*=9) formed only monomorphism. Derivative **1b** (*n*=12) have a highest clearing temperature at T_{cl}=217.6 °C, as well as a widest temperature range of mesophases of ΔT_{SmC}=112.4 °C among all derivatives **1a**–**e**. The mesophase was identified as smectic C phase based textures observed under optical microscope. Derivatives **1c** (*n*=6, 8, 10, 12) formed polymorphism and derivatives **1c** (*n*=14) formed monomorphism. Also, nematic phases

Table 2
The transition temperatures and enthalpies[a] of compounds **1a**–**e**

1a; *m*=5, *n*=6					Cr	$\underset{110.4(37.5)}{\overset{128.9(39.1)}{\rightleftharpoons}}$	I
8			Cr	$\underset{102.4(34.0)}{\overset{121.7(34.5)}{\rightleftharpoons}}$	SmX	$\underset{131.4(7.28)}{\overset{133.3(7.36)}{\rightleftharpoons}}$	I
10			Cr	$\underset{91.0(27.1)}{\overset{112.6(28.0)}{\rightleftharpoons}}$	SmX	$\underset{143.1(10.3)}{\overset{146.0(10.7)}{\rightleftharpoons}}$	I
12			Cr	$\underset{94.2(27.4)}{\overset{108.8(27.1)}{\rightleftharpoons}}$	SmX	$\underset{149.3(12.9)}{\overset{150.8(13.1)}{\rightleftharpoons}}$	I
14			Cr	$\underset{97.3(24.5)}{\overset{109.7(24.7)}{\rightleftharpoons}}$	SmX	$\underset{152.5(9.17)}{\overset{153.7(9.15)}{\rightleftharpoons}}$	I
1b; *m*=6, *n*=12			Cr	$\underset{98.2(29.8)}{\overset{126.6(39.5)}{\rightleftharpoons}}$	SmC	$\underset{210.6(19.3)}{\overset{217.6(22.3)}{\rightleftharpoons}}$	I
1c; *m*=7, *n*=6	Cr	$\underset{88.1(19.2)}{\overset{125.2(18.2)}{\rightleftharpoons}}$	SmA	$\underset{121.0(0.09)}{\overset{130.9(0.01)}{\rightleftharpoons}}$	N	$\underset{162.2(0.88)}{\overset{169.2(0.68)}{\rightleftharpoons}}$	I
8	Cr	$\underset{87.6(12.8)}{\overset{109.3(12.4)}{\rightleftharpoons}}$	SmA	$\underset{119.0}{\overset{127.0}{\rightleftharpoons}}$ [b]	N	$\underset{140.1(0.58)}{\overset{153.0(1.00)}{\rightleftharpoons}}$	I
10	Cr	$\underset{86.2(14.3)}{\overset{110.7(12.0)}{\rightleftharpoons}}$	SmC	$\underset{114.8(2.63)}{\overset{128.1(1.64)}{\rightleftharpoons}}$	N	$\underset{138.0}{\overset{142.0}{\rightleftharpoons}}$ [b]	I
12	Cr	$\underset{86.0(21.8)}{\overset{105.2(23.3)}{\rightleftharpoons}}$	SmC	$\underset{138.0(9.01)}{\overset{144.6(9.45)}{\rightleftharpoons}}$	N	$\underset{142.5(1.72)}{\overset{147.8(1.65)}{\rightleftharpoons}}$	I
14			Cr	$\underset{84.2(34.7)}{\overset{99.4(34.5)}{\rightleftharpoons}}$	SmC	$\underset{138.8(14.6)}{\overset{141.4(15.7)}{\rightleftharpoons}}$	I
1d; *m*=8, *n*=12			Cr	$\underset{104.9(46.2)}{\overset{130.5(46.5)}{\rightleftharpoons}}$	SmC	$\underset{182.8(16.3)}{\overset{187.4(13.5)}{\rightleftharpoons}}$	I
1e; *m*=9, *n*=6			Cr	$\underset{124.3(51.8)}{\overset{133.9(52.2)}{\rightleftharpoons}}$	N	$\underset{152.0(1.54)}{\overset{152.8(1.62)}{\rightleftharpoons}}$	I
8			Cr	$\underset{103.5(40.9)}{\overset{124.7(43.0)}{\rightleftharpoons}}$	N	$\underset{158.3(1.05)}{\overset{159.4(1.15)}{\rightleftharpoons}}$	I
10			Cr	$\underset{121.0(52.5)}{\overset{130.1(52.6)}{\rightleftharpoons}}$	N	$\underset{153.5(1.41)}{\overset{153.9(1.23)}{\rightleftharpoons}}$	I
12			Cr	$\underset{101.4(28.0)}{\overset{119.8(29.6)}{\rightleftharpoons}}$	N	$\underset{133.5(1.15)}{\overset{134.3(1.27)}{\rightleftharpoons}}$	I
14			Cr	$\underset{112.0(32.2)}{\overset{125.0(33.0)}{\rightleftharpoons}}$	N	$\underset{127.3(1.19)}{\overset{136.3(1.21)}{\rightleftharpoons}}$	I

[a] *n*=Carbon lengths in the alkoxy groups. Cr=Crystal, SmX=smectic X, SmC=smectic C, SmA=smectic A, and N=nematic phases. Temperatures (°C) and enthalpies (kJ/mol) were obtained by DSC at a scan rate of 10.0 °C/min.

[b] Observed by polarizing optical microscope.

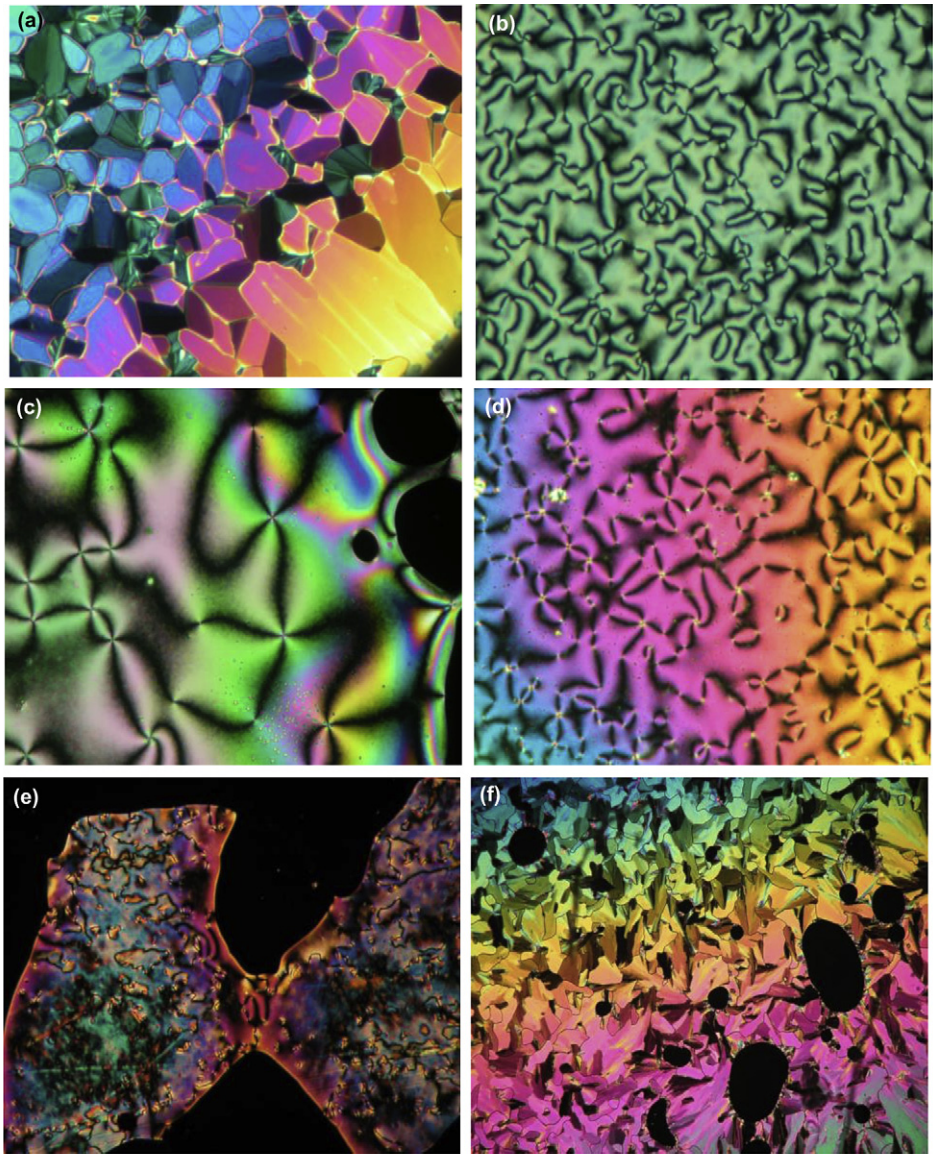


Fig. 1. Optical textures observed. (a) Top left: SmX phase by **1a** (m=5, n=8) at 121 °C; (b) top right: N phase by **1c** (m=7, n=8) at 139 °C; (c) central left: N phase by **1e** (m=9, n=6) at 151 °C; (d) central right: N phase by **1e** (m=9, n=12) at 132 °C; (e) bottom left: N phase at by **1c** (m=7, n=6) at 150 °C; (f) bottom right: SmC phase by **1c** (m=7, n=12) at 110 °C.

were observed for all derivatives with an odd spacer **1c** (except for n=14) and **1e** (m=9), whereas smectic C phases were obtained for other derivatives **1b** (m=6) and **1d** (m=8) with an even spacer. The difference on the formation of phases was correlated with the conformations displayed by odd–even spacers, which was also observed in other similar mesogenic twins. For the compounds **1c** (m=7; n=6, 8, 10, 12, 14) the clearing temperatures were decreased with the carbon numbers of the terminal alkyl chains, i.e., T_{cl}=169.2 (n=6)>141.4 °C (n=14), however, the melting temperatures remained at 125.2 °C (n=10)–99.4 °C (n=14). The mesophase temperatures were ranged; ΔT_M=51.8 (n=10)–74.1 (n=6) °C on cooling process. Two derivatives **1c** with shorter carbon lengths (n=6, 8) exhibited nematic phases at higher temperature and smectic A phases at lower temperatures, whereas two other derivatives with longer carbon lengths (n=10, 12) exhibited nematic phases at higher temperature and smectic C phases at lower temperatures. The derivative **1c** with longest carbon lengths (n=14) formed only smectic C phases. The dependence of phase with carbon lengths was probably attributed to an enhanced dispersive interaction or van der Waals between the terminal alkoxy chains as carbon lengths increases. The mesophases were characterized and identified by microscope. The phases were identified as nematic, smectic A and smectic C phases, and typical textures described as focal-conic or Schlieren domains (Fig. 1) were easily observed under optical polarized microscope when cooling from their isotropic liquids. A texture appeared as focal-conic characterized for SmA phases was also confirmed by its homeotropic domain, which were not observed in SmC phases. A relatively smaller enthalpy of ΔH=0.58–1.72 kJ/mol on cooling process for compounds **1c** for the transition of I→N phase and an enthalpy of ΔH=0.09–1.82 kJ/mol for the transition of N→SmA phases were obtained. In contrast, a larger enthalpy of ΔH=1.64–9.45 kJ/mol for the transition of SmC→N phases was obtained for all derivatives **1c**. A large enthalpy of ΔH=15.7 kJ/mol was also obtained for **1c** (n=14).

Derivative **1d** (m=8, n=12) formed smectic C phase with a temperature range of ΔT_{SmC}=77.9 °C. The temperature range of mesophase was relatively wider than those of other derivatives **1c** (ΔT=56.5 °C) and **1e** (ΔT=32.1 °C) with a carbon length n=12. When spacer was elongated to an odd m=9, nematic phases were solely observed. All clearing temperatures were ranged in T_{cl}=134.3 (n=12)–159.4 (n=8) °C. Compared to all other three derivatives **1b**–**d**, the temperature range of mesophases was apparently reduced to ca. ΔT_N=10.3 (n=14)–34.8 °C (n=6). The melting temperatures were slightly higher than those of derivatives **1c**–**d**, whereas, the clearing temperatures remained at T_{cl}=159.4 (n=8)–136.3 °C (n=14). The thermal stability of compounds **1a**–**d** (all n=12) was also characterized by thermogravimetric analyses (TGA), as shown in Fig. 2. Two compounds showed excellent thermal stability above their clearing temperature. For example, the decomposition temperatures for a 5% weight loss for **1a** (m=5, n=12), **1b** (m=6, n=12), **1c** (m=7, n=12), and **1d** (m=8, n=12) were obtained at T_d=346.0 °C, 337.0 °C, 342.0 °C, and 339.0 °C.

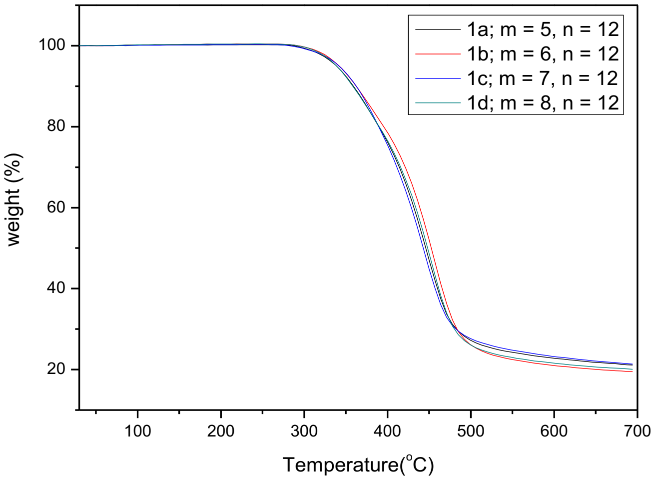


Fig. 2. The TGA thermographs of compounds **1a**–**d**.

2.3. Odd–even effect

The difference on the formation of phases in these twins **1a**–**e** was attributed to the conformations displayed by odd–even spacers, which was also observed in other similar mesogenic twins. Molecules or twins with an even spacer displayed a more linear shaped or conformation, often giving smectic C phases (Fig. 3). It has been known that spacers with even parity have more conformers, which allowed parallel arrangements between cores, whereas odd spacers possess more conformers, which often resulted in bent configuration. The odd–even effect on the phase temperatures; both melting and clearing temperatures was also examined.

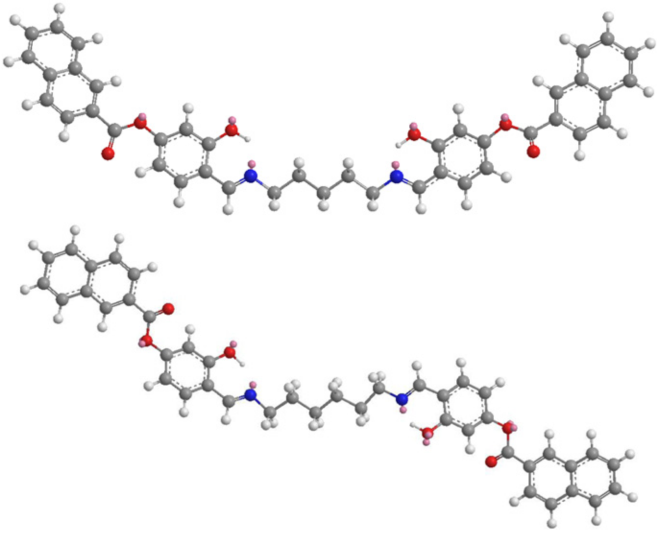


Fig. 3. Schematic ball-and-stick representation of the all-trans conformations. Top: bent-shaped by an odd-**1a** (m=5) and bottom: linear-shaped by an even membered dimer **1b** (m=6).

The relationship plot between the melting temperatures, clearing temperatures, and the temperature range for all twins **1a**–**e** was given in Fig. 4. For detail comparison, the dependence of melting and clearing temperatures on the spacer lengths (m=5, 6, 7, 8, 9) in compounds **1a**–**e** (all with carbon length n=12 in the terminal alkoxy groups) was given in Fig. 5. Both derivatives with even spacer cleared at higher temperatures, i.e., T_{cl}=217.6 °C (m=6, n=12) and 187.4 °C (m=8, n=12) than those of derivatives with odd spacer (m=7, 9), i.e., T_{cl}=147.8 °C (m=7, n=12) and 134.3 °C (m=9, n=12). Derivatives **1b**, **d** with even spacers (m=6, 8) formed smectic phase, whereas derivatives **1c**, **e** with odd spacers (m=7, 9) exhibited nematic and smectic C phase. The derivative **1b** (n=12) have a highest clearing temperature at T_{cl}=217.6 °C and a widest temperature range of ΔT_{SmC}=112.4 °C among all twins **1a**–**e**. When

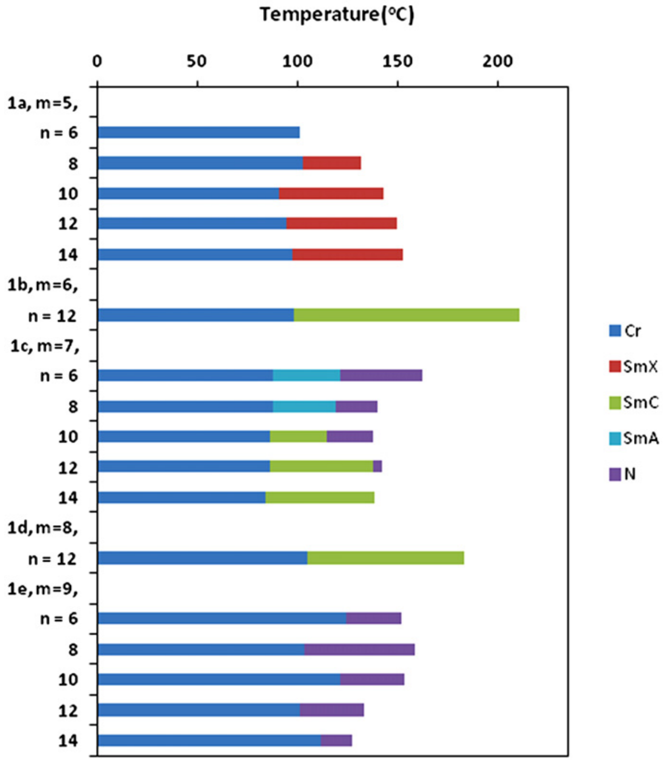


Fig. 4. Bar graphs showing the phase behavior of compounds **1a**–**e**. All temperatures were taken from heating process.

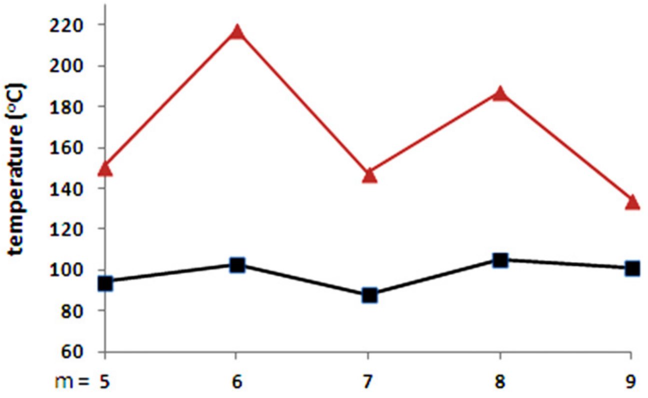


Fig. 5. Dependence of melting and clearing temperatures on the spacer lengths (m=5, 6, 7, 8, 9) in compounds **1a**–**e** (all with carbon length n=12 in the terminal alkoxy groups). All temperatures were taken from cooling process.

compounds with even carbon spacer and molecules were considered in all-trans conformations, the overall molecules were more likely linear, resulting in a better packing in mesophases. Therefore, their clearing temperatures were often much higher than those of compounds with odd carbon spacer, in which all molecules were considered as more bent-shaped.

2.4. Variable–temperature X-ray diffraction data

Three molecular organizations proposed in such twins were known; monolayers, interdigitated layers, and intercalated layers, as shown in Fig. 6. Symmetric twins adopt monolayers or interdigitated layers, whereas unsymmetric twins favor intercalated layers. The powder X-ray diffraction experiments of two derivatives **1a** (m=5, n=8) and **1c** (m=7, n=14) were performed to confirm the layer structures. The X-ray diffraction data were summarized in Table 3. Derivative **1a** (m=5, n=8) gave a more ordered diffraction pattern; two strong and two weaker diffraction peaks, appeared at a d-spacing of 49.51 (49.5), 35.02 and 24.71 Å were observed, as shown Fig. 7. This diffraction pattern was typically characteristic of layer structures observed for a more highly ordered SmX phases. The exact mesophase was not attempted to identify. In contrast, **1c** (m=7, n=14) displayed a diffraction pattern with one strong peak at 56.68 Å and one very weak at 28.41 Å, and these two diffraction peaks at lower angle were assigned as Mill indices 001 and 002. This diffraction pattern was typically characteristic of layer structures observed for SmC phases. A very broad and very weak peak at 4.44–4.61 Å was also observed, and this peak was assigned to the molten alkoxyl chains. The d-spacing of two compounds; 49.51 Å and 56.68 Å was well correlated with the calculated molecular lengths of 54.0 Å and 67.6 Å. Two structures in such layer mesophases were proposed for symmetric twins; intercalated and non-intercalated (or monolayer). In intercalated phase the d-spacing value was approximately equal to a half of molecular length $d \sim (1/2)L$ whereas d-spacing was equal to molecular length $d=L$ in non-intercalated structure. Interdigitated layer structures were ruled out in this system. In many mesogenic twin systems, most dimeric molecules exhibiting smectic phases adopted intercalated arrangements. In contrast, the dimeric molecules **1c–e** will form monolayer arrangement when $d/l=\sim 1.0$. A value of d/l=0.92 (**1a**; m=5, n=8)–0.84 (**1c**; m=7, n=14) was obtained. Therefore, a monolayer structure[18] in mesophase was proposed.

Table 3
A summary of powder XRD diffraction peaks of compounds **1a** and **1c**

Compds	Mesophases	Molecular length (Å)	d-Spacing obs. (calcd)	Miller indices	Aspect ratio d/l
1a (m=5, n=8)	SmX	54.0	49.51 (49.5)	001	0.92
		35.02 (35.02)	100		
		24.71 (24.75)	001		
		17.51 (17.51)	200		
1c (m=7, n=14)	SmC	67.6	56.68 (56.68)	001	0.84
			28.41 (28.34)	002	

3. Conclusions

A new series of mesogenic twins with different spacer lengths (m=5, 6, 7, 8, 9) was prepared and studied. These dimeric twins were constructed by mesogenic salicylaldimines linked with terminal naphthalene as core. The two naphthalene moieties incorporated might enhance $\pi-\pi$ interaction between smectic layers. All the derivatives **1a** with shorter spacers (m=5) were not mesogenic. On the other hand, all other derivatives **1b–e** with longer spacers (m=6, 7, 8, 9) formed nematic, smectic A or smectic C phases. The temperatures were relatively narrow in all derivatives. An odd–even effect both on the melting and isotropization temperatures was observed. A monolayer structure in this type of dimeric twin liquid crystals was proposed.

4. Experimental

4.1. General

All chemicals and solvents were reagent grades from Aldrich Chemical Co. Solvents used were dried by standard technique. ^{1}H 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. Elemental analysis for carbon, hydrogen, and nitrogen were conducted at Instrumentation Center, National Taiwan University on a Heraeus CHN–O-Rapid elemental analyzer. The powder diffraction data were collected from the Wiggler-A beamline of the National Synchrotron Radiation Research Center

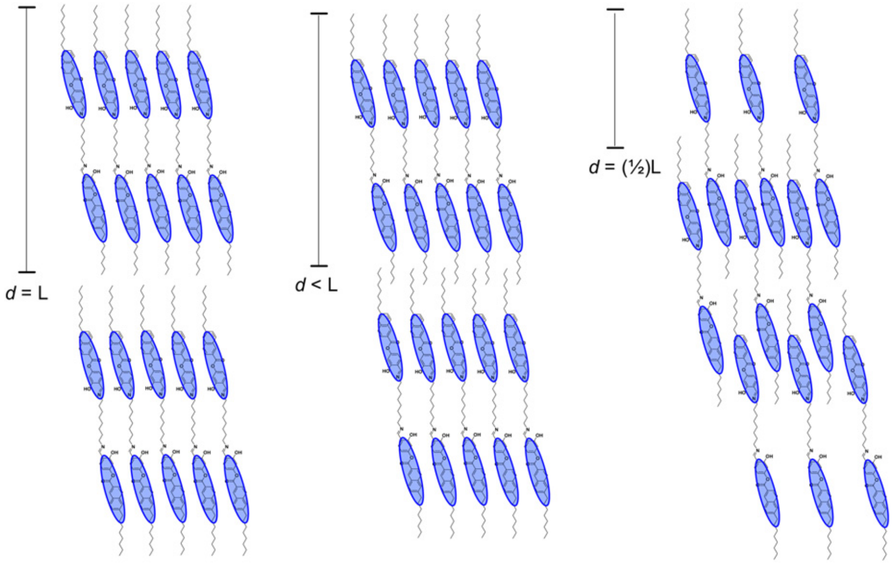


Fig. 6. The monolayer arrangements in SmC phases proposed for compounds **1d** (m=8) with an aspect ratio of d/L ~1.0. The terminal alkoxyl chains are not interdigitated.

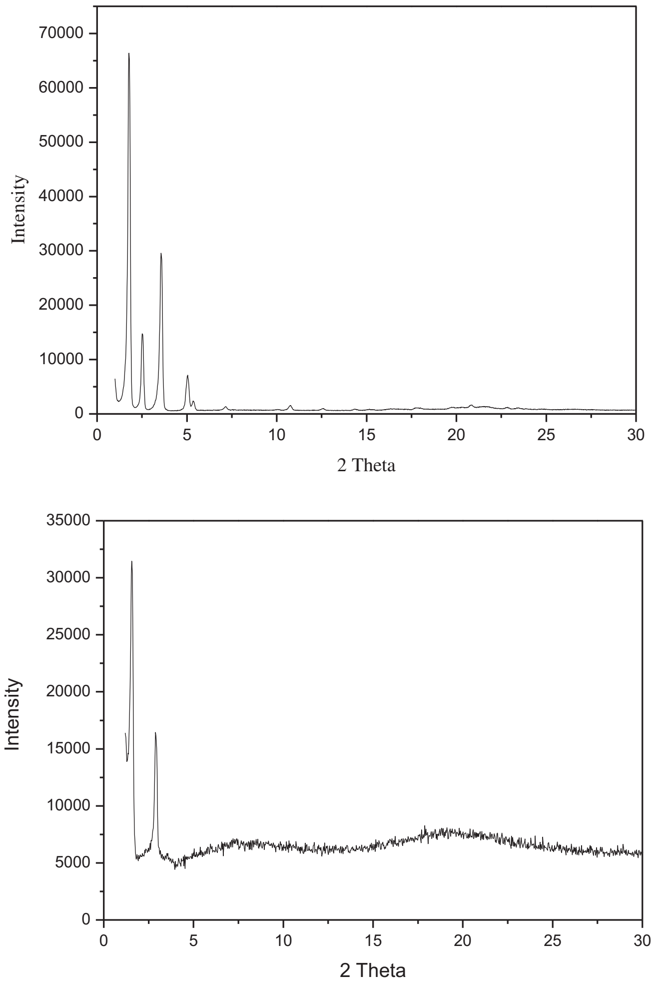


Fig. 7. Variable temperature powder X-ray diffraction plots of compounds. Top plot: SmX phase by **1a** (m=5, n=8) at 120 °C (top plot) and bottom: SmC phase by **1c** (m=7, n=14) at 120 °C (bottom plot).

(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=10–25° step^{-1} s^{-1} and a gas flow heater was used to control the temperature. The powder samples were charged in Lindemann capillary tubes (80 mm long and 0.01 mm thick) from Charles Supper Co. with an inner diameter of 1.0 mm.

4.2. Synthetic preparation of compounds 1a–e

4.2.1. 6-Hydroxy-naphthalene-2-carboxylic acid methyl ester. The solution of 6-hydroxy-2-naphthaoic acid (10.0 g, 0.053 mol) dissolved in CH_3OH was slowly added 2.0 mL of concentrated H_2SO_4 and the solution was refluxed for 24 h. The solution was cooled to room temperature, and the solids as light brown solids were collected. The solids were purified by recrystallization from methanol. Yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.95 (s, 3H, $-OCH_3$), 5.74 (s, 1H, Ar–OH), 7.15 (d, 2H, Ar–H, J=7.62 Hz), 7.67 (d, 1H, Ar–H, J=8.58 Hz), 7.83 (d, 1H, Ar–H, J=9.69 Hz), 7.98 (d, 1H, Ar–H, J=8.72 Hz), 8.51 (s, 1H, Ar–H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 50.0, 109.3, 118.5, 125.3, 125.9, 126.5, 127.9, 130.7, 131.2, 136.4, 155.6, 167.0.

4.2.2. 6-Dodecyloxynaphthalene-2-carboxylic acid methyl ester (n=12). The mixture of 6-hydroxy-naphthalene-2-carboxylic acid methyl ester (5.0 g, 0.025 mol), 1-bromododecane (6.16 g, 0.025 mol), K_2CO_3 (6.83 g, 0.049 mol), and KI was gently refluxed in dried for 24 h under nitrogen atmosphere. The solution was concentrated and extracted with 100 mL of CH_2Cl_2/H_2O (1/1). The organic layers were collected and dried over anhydrous $NaSO_4$. The products isolated as white solids were obtained after recrystallization from CH_3COCH_3/H_2O. Yield 88%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85–0.88 (t, 3H, $-CH_3$, J=6.6 Hz), 1.29–1.50 (m, 18H, $-CH_2$), 1.83–1.85 (m, 2H, $-CH_2$), 4.08–4.11 (t, 2H, $-OCH_2$, J=6.5 Hz), 7.14 (s, 1H, Ar–H), 7.18–7.20 (d, 1H, Ar–H, J=8.9 Hz), 7.73–7.75 (d, 1H, Ar–H, J=8.6 Hz), 7.83–7.85 (d, 1H, Ar–H, J=8.9 Hz), 8.04–8.06 (d, 1H, Ar–H, J=8.8 Hz), 8.59 (s, 1H, Ar–H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.91, 22.55, 26.05, 29.15, 29.28, 29.35, 31.75, 68.30, 106.72, 119.97, 121.29, 124.16, 126.05, 126.85, 127.85, 130.95, 131.80, 137.75, 159.51.

4.2.3. 6-(Dodecyloxy)naphthalene-2-carboxylic acid ***3*** *(n=12).* White solids, yield 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 3H, $-CH_3$, J=6.69 Hz), 1.26–1.50 (m, 18H, $-CH_2$), 1.78–1.84 (m, 2H, $-CH_2$), 4.09 (t, 2H, $-OCH_2$, J=6.53 Hz), 7.13 (s, 1H, Ar–H), 7.16 (d, 1H, Ar–H, J=11.34 Hz), 7.70 (d, 1H, Ar–H, J=8.64 Hz), 7.81 (d, 1H, Ar–H, J=8.97 Hz), 7.99 (d, 1H, Ar–H, J=10.12 Hz), 8.49 (s, 1H, Ar–H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.92, 22.58, 26.05, 28.84, 29.17, 29.25, 29.32, 29.47, 29.52, 29.57, 31.85, 68.26, 106.68, 119.76, 125.66, 125.88, 126.64, 127.92, 130.65, 130.74, 137.21, 159.11, 166.90.

4.2.4. 6-Dodecyloxynaphthalene-2-carboxylic acid 4-formyl-3-hydro xyphenyl ester ***2*** *(n=12).* The solution of 6-dodecyloxynaphthalene-2-carboxylic acid (2.00 g, 6.0 mmol), 4-dimethyl aminopyridine (DMAP; 0.89 g, 7 mmol), and 2,4-dihydroxybenzoaldehyde (0.84 g, 0.006 mol) was stirred at ice bath temperature for 30 min. The solution was warmed up to room temperature. The solution was then added *N,N′*-dicyclohexylcarbodiimide (DCC; 1.51 g, 7.0 mmol), and stirred at room temperature for 24 h. The insoluble solids were filtered off. The solution was concentrated to give off-white solids and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2; 1/1). White solids were obtained after recrystallization from CH_2Cl_2/CH_3OH. Yield 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86–0.90 (t, 3H, $-CH_3$, J=6.7 Hz), 1.27–1.56 (m, 18H, $-CH_2$), 1.83–1.86 (m, 2H, $-OCH_2$), 4.08–4.10 (t, 2H, $-OCH_2$, J=6.5 Hz), 6.91 (s, 1H, Ar–H), 6.93–6.96 (d, 1H, Ar–H, J=8.4 Hz), 7.15 (s, 1H, Ar–H), 7.20–7.22 (d, 1H, Ar–H, J=8.9 Hz), 7.60–7.62 (d, 1H, Ar–H, J=8.4 Hz), 7.77–7.79 (d, 1H, Ar–H, J=8.6 Hz), 7.85–7.87 (d, 1H, Ar–H, J=8.9 Hz), 8.08–8.10 (d, 1H, Ar–H, J=8.6 Hz), 8.65 (s, 1H, Ar–H), 9.88 (s, 1H, –CHO), 11.25 (s, 1H, Ar–OH). ^{13}C NMR (125 MHz, $CDCl_3$): 14.11, 22.67, 26.10, 29.15, 29.25, 29.37, 31.83, 68.28, 106.48, 110.94, 114.18, 118.68, 120.33, 123.51, 126.00, 127.16, 127.75, 131.04, 132.06, 134.98, 137.86, 157.93, 159.70, 163.25, 164.48, 195.50.

4.2.5. N,N-(1,5-Pentylene)-bis(4-dodecyloxynaphthalenelidenimine) ***1a*** *(m=5, n=12).* The solution of 6-dodecyloxynaphthalene-2-carboxylic acid 3-hydroxy-4-(2-methoxy-ethyl)-phenyl ester (0.50 g, 0.94 mmol) dissolved in 10.0 mL of absolute ethanol was added a few drops of CH_3COOH and 1,5-diaminopentane (0.047 g, 0.46 mmol). The solution was refluxed for 24 h. The yellow solids were collected. The products isolated as yellow solids were obtained by recrystallization from CH_2Cl_2/hexane. Yield 88%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 6H, $-CH_3$, J=6.72 Hz), 1.25–1.27 (m, 36H, $-CH_2$), 1.46–1.51 (m, 4H, $-CH_2$), 1.78–1.86 (m, 8H, $-CH_2$), 3.61 (t, 4H, $-CH_2NCH$, J=6.57 Hz), 4.09 (t, 4H, $-OCH_2$, J=6.48 Hz), 6.76 (s, 2H, Ar–H), 6.85 (s, 2H, Ar–H), 7.14 (s, 2H, Ar–H), 7.20 (s, 2H, Ar–H), 7.27 (d, 2H, Ar–H, J=8.4 Hz), 7.75 (d, 2H, Ar–H, J=8.6 Hz), 7.84 (d, 2H, Ar–H, J=8.9 Hz), 8.09 (d, 2H, Ar–H, J=8.6 Hz), 8.10 (d, 2H, Ar–H, J=8.6 Hz), 8.33 (s, 2H, –NCH), 8.65 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.13, 22.70, 24.67, 26.10, 29.17, 29.36, 29.41, 29.60, 29.62, 29.65, 29.68, 30.47, 31.93, 58.89, 68.24, 106.44, 110.65, 112.30, 116.64, 120.15, 124.12, 126.11, 127.00, 127.78, 131.00, 131.82, 132.12, 137.66, 154.23, 159.48, 163.41, 164.11, 165.05. Anal. Calcd for $C_{65}H_{82}N_2O_8$: C, 76.59; H, 8.11. Found C, 76.54; H, 8.22.

4.2.6. N,N-(1,5-Pentylene)-bis(4-hexyloxynaphthalenelidenimine) ***1a*** *(m=5, n=6).* Light yellow solids, yield 77%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.93 (t, 6H, $-CH_3$, J=6.72 Hz), 1.37–1.40 (m, 12H, $-CH_2$), 1.51–1.53 (m, 4H, $-CH_2$), 1.75–1.79 (m, 4H, $-CH_2$), 1.84–1.90 (m, 8H, $-CH_2CH_2$), 3.62 (t, 4H, $-CH_2N{=}CH$, J=6.57 Hz), 4.11 (t, 4H, $-OCH_2$, J=6.54 Hz), 6.79 (d, 2H, Ar–H), 6.86 (s, 2H, Ar–H), 7.16 (s, 2H, Ar–H), 7.22 (d, 2H, Ar–H, J=8.66 Hz), 7.28 (d, 2H, Ar–H, J=8.39 Hz), 7.77 (d, 2H, Ar–H, J=8.66 Hz), 7.86 (d, 2H, Ar–H, J=8.98 Hz), 8.12 (d, 2H, Ar–H, J=7.30 Hz), 8.34 (s, 2H, $-N{=}CH$), 8.67 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.13, 22.95, 24.98, 26.10, 29.46, 30.79, 31.92, 59.19, 68.56, 106.78, 110.97, 112.61, 116.97, 120.47, 124.46, 126.44, 127.34, 128.11, 131.33, 132.14, 132.44, 137.99, 154.56, 159.81, 163.74, 164.44, 165.36. Anal. Calcd for $C_{53}H_{58}N_2O_8$: C, 74.80; H, 6.87. Found C, 74.31; H, 6.87.

4.2.7. N,N-(1,5-Pentylene)-bis(4-octyloxynaphthalenelidenimine) ***1a*** *(m=5, n=8).* Light yellow solids, yield 79%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, 6H, $-CH_3$, J=6.16 Hz), 1.29–1.37 (m, 16H, $-CH_2CH_3$), 1.47–1.51 (m, 6H, $-OCH_2CH_2$), 1.74–1.77 (m, 4H, $-CH_2$), 1.83–1.86 (m, 4H, $-CH_2$), 3.60 (t, 4H, $-CH_2-N{=}CH$, J=6.44 Hz), 4.08 (t, 4H, $-OCH_2$, J=6.48 Hz), 6.76 (d, 2H, Ar–H), 6.77 (s, 2H, Ar–H), 7.14 (s, 2H, Ar–H), 7.18 (d, 2H, Ar–H, J=8.66 Hz), 7.20 (d, 2H, Ar–H, J=8.39 Hz), 7.26 (d, 2H, Ar–H, J=8.66 Hz), 7.75 (d, 2H, Ar–H, J=8.98 Hz), 8.11 (d, 2H, Ar–H, J=7.30 Hz), 8.32 (s, 2H, $-N{=}CH$), 8.65 (s, 2H, Ar–H) ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.15, 22.70, 24.67, 26.12, 29.19, 29.28, 29.40, 30.48, 31.85, 58.88, 68.24, 106.44, 110.65, 112.29, 116.65, 120.16, 124.12, 126.12, 127.02, 128.78, 131.00, 131.82, 132.14, 137.66, 154.23, 159.23, 159.48, 163.42, 164.12, 165.04. Anal. Calcd for $C_{57}H_{66}N_2O_8$: C, 75.47; H, 7.33. Found C, 75.35; H, 7.38.

4.2.8. N,N-(1,5-Pentylene)-bis(4-decanoxynaphthalenelidenimine) ***1a*** *(m=5, n=10).* Light yellow solids, yield 77%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, 6H, $-CH_3$, J=6.21 Hz), 1.29–1.38 (m, 20H, $-CH_2$), 1.48–1.53 (m, 6H, $-OCH_2$), 1.76–1.79 (m, 4H, $-CH_2CH_2$), 1.85–1.88 (m, 4H, $-CH_2$), 3.62 (t, 4H, $-CH_2-N{=}CH$, J=6.52 Hz), 4.11 (t, 4H, $-OCH_2$, J=6.49 Hz), 6.77 (d, 2H, Ar–H), 6.79 (s, 2H, Ar–H), 7.16 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=8.66 Hz), 7.22 (d, 2H, Ar–H, J=8.39 Hz), 7.28 (d, 2H, Ar–H, J=8.66 Hz), 7.77 (d, 2H, Ar–H, J=8.98 Hz), 8.13 (d, 2H, Ar–H, J=7.30 Hz), 8.34 (s, 2H, $-N{=}CH$), 8.67 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.45, 23.02, 24.99, 26.43, 29.50, 29.66, 29.74, 29.90, 29.92, 30.79, 32.24, 59.20, 68.56, 106.77, 110.97, 112.61, 116.96, 120.47, 124.45, 126.44, 127.34, 128.11, 131.33, 132.14, 132.44, 137.98, 154.56, 159.80, 163.75, 164.44, 165.37. Anal. Calcd for $C_{61}H_{74}N_2O_8$: C, 76.06; H, 7.74. Found C, 75.92; H, 7.83.

4.2.9. N,N-(1,5-Pentylene)-bis(4-tetradecanoxynaphthalenelidenimine) ***1a*** *(m=5, n=14).* Light yellow solids, yield 74%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.88 (t, 6H, $-CH_3$, J=6.52 Hz), 1.27–1.39 (m, 44H, $-CH_2$), 1.48–1.51 (m, 6H, $-CH_2$), 1.76–1.79 (m, 4H, $-CH_2$), 1.85–1.88 (m, 4H, $-CH_2CH_2$), 3.62 (t, 4H, $-CH_2-N{=}CH$, J=6.40 Hz), 4.11 (t, 4H, $-OCH_2$, J=6.48 Hz), 6.77 (d, 2H, Ar–H), 6.79 (s, 2H, Ar–H), 7.16 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=8.66 Hz), 7.22 (d, 2H, Ar–H, J=8.39 Hz), 7.28 (d, 2H, Ar–H, J=2.39 Hz), 7.77 (d, 2H, Ar–H, J=8.98 Hz), 8.13 (d, 2H, Ar–H, J=7.30 Hz), 8.34 (s, 2H, $-N{=}CH$), 8.67 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.46, 23.03, 24.99, 26.43, 29.51, 29.70, 29.74, 29.93, 29.95, 30.03, 30.80, 32.27, 59.21, 68.56, 106.79, 110.98, 112.62, 116.97, 120.48, 124.47, 127.34, 128.12, 131.33, 132.14, 132.44, 137.99, 154.57, 159.82, 163.75, 164.44, 165.37. Anal. Calcd for $C_{69}H_{90}N_2O_8$: C, 77.06; H, 8.43. Found C, 77.56; H, 8.45.

4.2.10. N,N-(1,5-Hextylene)-bis(4-dodecyloxynaphthalenelidenimine) ***1b*** *(m=6, n=12).* Light yellow solids, yield 84%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, 6H, $-CH_3$, J=6.62 Hz), 1.27–1.39 (m, 36H, $-CH_2$), 1.46–1.53 (m, 8H, $-CH_2$), 1.73–1.75 (m, 4H, $-CH_2$), 1.84–1.88 (m, 4H, $-CH_2CH_2$), 3.61 (t, 4H, $-CH_2-N{=}CH$, J=6.57 Hz), 4.11 (t, 4H, $-OCH_2$, J=6.51 Hz), 6.77 (d, 2H, Ar–H), 6.79 (s, 2H, Ar–H), 7.17 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=2.39 Hz), 7.22 (d, 2H, Ar–H, J=8.39 Hz), 7.28 (d, 2H, Ar–H, J=8.39 Hz), 7.78 (d, 2H, Ar–H, J=8.65 Hz), 7.87 (d, 2H, Ar–H, J=8.65 Hz), 8.12 (d, 2H, Ar–H, J=1.54 Hz), 8.34 (s, 2H, $-N{=}CH$), 8.68 (s, 2H, Ar–H) ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.45, 23.02, 26.42, 27.12, 29.49, 29.68, 29.73, 29.92, 29.94, 29.97, 30.00, 30.97, 32.25, 59.16, 68.57, 106.79, 110.99, 112.54, 116.97, 120.48, 124.47, 128.12, 131.33, 132.14, 132.42, 137.99, 154.57, 159.81, 163.91, 164.31, 165.37. Anal. Calcd for $C_{66}H_{84}N_2O_8$: C, 76.71; H, 8.19. Found C, 76.88; H, 8.21.

4.2.11. N,N-(1,7-Heptylene)-bis(4-hexyloxynaphthalenelidenimine) ***1c*** *(m=7, n=6).* Light yellow solids, yield 74%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.94 (t, 6H, $-CH_3$, J=6.52 Hz), 1.37–1.40 (m, 15H, $-CH_2$), 1.41–1.53 (m, 4H, $-CH_2$), 1.70–1.71 (m, 4H, $-CH_2$), 1.83–1.89 (m, 4H, $-CH_2CH_2$), 3.58 (t, 4H, $-CH_2-N{=}CH$, J=6.52 Hz), 4.10 (t, 4H, $-OCH_2$, J=6.42 Hz), 6.77 (d, 2H, Ar–H), 6.88 (s, 2H, Ar–H), 7.16 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=2.40 Hz), 7.22 (d, 2H, Ar–H, J=6.62 Hz), 7.27 (d, 2H, Ar–H, J=8.40 Hz), 7.77 (d, 2H, Ar–H, J=8.66 Hz), 7.86 (d, 2H, Ar–H, J=8.98 Hz), 8.12 (d, 2H, Ar–H, J=1.52 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.68 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.33, 22.88, 26.04, 27.29, 29.26, 29.40, 30.96, 31.86, 59.13, 68.49, 106.73, 110.94, 112.41, 116.40, 120.41, 124.41, 126.36, 127.28, 128.05, 131.25, 132.05, 132.36, 137.93, 154.52, 159.75, 163.97, 164.17, 165.26. Anal. Calcd for $C_{55}H_{62}N_2O_8$: C, 75.14; H, 7.11. Found C, 75.76; H, 6.92.

4.2.12. N,N-(1,7-Heptylene)-bis(4-octyloxynaphthalenelidenimine) ***1c*** *(m=7, n=8).* Light yellow solids, yield 83%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.88 (t, 6H, $-CH_3$, J=6.58 Hz), 1.37–1.39 (m, 20H, $-CH_2$), 1.40–1.51 (m, 4H, $-CH_2$), 1.69–1.83 (m, 4H, $-CH_2$), 1.85–1.87 (m, 4H, $-CH_2$), 3.58 (t, 4H, $-CH_2-N{=}CH$, J=6.67 Hz), 4.09 (t, 4H, $-OCH_2$, J=6.51 Hz), 6.74 (d, 2H, Ar–H), 6.84 (s, 2H, Ar–H), 7.14 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=2.39 Hz), 7.22 (d, 2H, Ar–H, J=6.62 Hz), 7.27 (d, 2H, Ar–H, J=8.39 Hz), 7.76 (d, 2H, Ar–H, J=8.67 Hz), 7.85 (d, 2H, Ar–H, J=8.99 Hz), 8.11 (d, 2H, Ar–H, J=1.52 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.15, 22.70, 26.12, 27.05, 29.02, 29.18, 29.28, 29.39, 30.71, 31.85, 58.95, 68.24, 106.42, 110.71, 112.19, 116.64, 120.17, 124.12, 126.14, 127.02, 127.78, 131.02, 132.09, 137.66, 154.22, 159.48, 163.68, 163.89, 165.07. Anal. Calcd for $C_{59}H_{70}N_2O_8$: C, 75.77; H, 7.54. Found C, 75.96; H, 7.72.

4.2.13. N,N-(1,7-Heptylene)-bis(4-decanoxynaphthalenelidenimine) ***1c*** *(m=7, n=10).* Light yellow solids, yield 81%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.87 (t, 6H, $-CH_3$, J=6.34 Hz), 1.34–1.39 (m, 24H, $-CH_2$), 1.46–1.51 (m, 4H, $-CH_2$), 1.69–1.82 (m, 4H, $-CH_2$), 1.85–1.87 (m, 4H, $-CH_2$), 3.58 (t, 4H, $-CH_2-N{=}CH$, J=6.53 Hz), 4.08 (t, 4H, $-OCH_2$, J=6.45 Hz), 6.74 (d, 2H, Ar–H), 6.84 (s, 2H, Ar–H), 7.15 (s, 2H, Ar–H), 7.21 (d, 2H, Ar–H, J=2.39 Hz), 7.26 (d, 2H, Ar–H, J=6.39 Hz), 7.76 (d, 2H, Ar–H, J=8.77 Hz), 7.85 (d, 2H, Ar–H, J=8.97 Hz), 8.10 (d, 2H, Ar–H, J=8.50 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.16, 22.71, 26.12, 27.05, 29.02, 29.18, 29.36, 29.43, 30.60, 29.62, 31.71, 31.93, 58.94, 68.23, 106.42, 110.71, 112.19, 116.64, 120.17, 124.12, 126.13, 127.02, 127.78, 131.02, 131.83, 132.10, 137.66, 154.23, 159.48, 163.69, 163.90, 165.07. Anal. Calcd for $C_{63}H_{78}N_2O_8$: C, 76.33; H, 7.93. Found C, 76.58; H, 8.19.

4.2.14. N,N-(1,7-Heptylene)-bis(4-dodecyloxynaphthalenelidenimine) ***1c*** *(m=7, n=12).* Light yellow solids, yield 71%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.87 (t, 6H, $-CH_3$, J=6.43 Hz), 1.36–1.38 (m, 36H, $-CH_2$), 1.46–1.53 (m, 4H, $-CH_2$), 1.69–1.82 (m, 4H, $-CH_2$), 1.85–1.89 (m, 4H,

$-CH_2$), 3.60 (t, 4H, $-CH_2-N{=}CH$, J=6.37 Hz), 4.10 (t, 4H, $-OCH_2$, J=6.43 Hz), 6.75 (d, 2H, Ar−H), 6.86 (s, 2H, Ar−H), 7.17 (s, 2H, Ar−H), 7.22 (d, 2H, Ar−H, J=1.93 Hz), 7.30 (d, 2H, Ar−H, J=6.39 Hz), 7.78 (d, 2H, Ar−H, J=8.67 Hz), 7.87 (d, 2H, Ar−H, J=8.97 Hz), 8.12 (d, 2H, Ar−H, J=8.55 Hz), 8.33 (s, 2H, $-N{=}CH$), 8.67 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.46, 23.03, 26.43, 27.36, 29.33, 29.50, 29.69, 29.74, 29.93, 29.95, 29.98, 30.00, 31.02, 32.26, 59.24, 68.56, 106.77, 111.02, 112.50, 116.95, 120.48, 124.46, 126.45, 127.34, 128.11, 131.33, 132.14, 132.40, 137.99, 154.57, 159.81, 164.02, 164.22, 165.37. Anal. Calcd for $C_{67}H_{86}N_2O_8$: C, 76.33; H, 7.93. Found C, 76.58; H, 8.19.

4.2.15. N,N-(1,7-Heptylene)-bis(4-tetradecanoxynaphthalenelidenimine) ***1c*** *(m=7, n=14).* Light yellow solids, yield 82%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 6H, $-CH_3$, J=6.65 Hz), 1.36−1.39 (m, 44H, $-CH_2$), 1.46−1.52 (m, 4H, $-CH_2$), 1.69−1.70 (m, 4H, $-CH_2$), 1.83−1.88 (m, 4H, $-CH_2$), 3.58 (t, 4H, $-CH_2-N{=}CH$, J=6.59 Hz), 4.09 (t, 4H, $-OCH_2$, J=6.50 Hz), 6.74 (d, 2H, Ar−H), 6.83 (s, 2H, Ar−H), 7.17 (s, 2H, Ar−H), 7.20 (d, 2H, Ar−H, J=2.22 Hz), 7.27 (d, 2H, Ar−H, J=8.39 Hz), 7.76 (d, 2H, Ar−H, J=8.68 Hz), 7.85 (d, 2H, Ar−H, J=8.99 Hz), 8.09 (d, 2H, Ar−H, J=1.35 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.16, 23.72, 26.11, 27.05, 29.02, 29.17, 29.39, 29.43, 29.61, 29.64, 29.69, 29.71, 30.71, 31.95, 58.97, 68.23, 106.41, 110.70, 112.20, 116.64, 120.17, 124.12, 126.14, 127.02, 127.78, 131.02, 131.83, 132.09, 137.66, 154.21, 159.48, 163.66, 163.89, 165.07. Anal. Calcd for $C_{71}H_{94}N_2O_8$: C, 77.28; H, 8.59. Found C, 77.30; H, 8.77.

4.2.16. N,N-(1,8-Octylene)-bis(4-dodecyloxynaphthalenelidenimine) ***1d*** *(m=8, n=12).* Light yellow solids, yield 82%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, 6H, $-CH_3$, J=6.31 Hz), 1.37−1.39 (m, 44H, $-CH_2$), 1.49−1.53 (m, 4H, $-CH_2$), 1.68−1.72 (m, 4H, $-CH_2CH_2$), 1.84−1.88 (m, 4H, $-CH_2$), 3.59 (t, 4H, $-CH_2-N{=}CH$, J=6.67 Hz), 4.11 (t, 4H, $-OCH_2$, J=6.51 Hz), 6.76 (d, 2H, Ar−H), 6.86 (s, 2H, Ar−H), 7.17 (s, 2H, Ar−H), 7.22 (d, 2H, Ar−H, J=6.80 Hz), 7.28 (d, 2H, Ar−H, J=8.40 Hz), 7.78 (d, 2H, Ar−H, J=8.66 Hz), 7.87 (d, 2H, Ar−H, J=8.97 Hz), 8.12 (d, 2H, Ar−H, J=8.69 Hz), 8.33 (s, 2H, $-N{=}CH$), 8.68 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.45, 23.03, 26.42, 27.37, 29.50, 29.69, 29.73, 29.92, 29.94, 29.98, 30.00, 31.06, 32.25, 59.23, 68.56, 106.79, 111.03, 112.47, 116.96, 120.48, 124.47, 126.44, 127.34, 128.12, 131.33, 131.83, 132.14, 132.38, 137.99, 154.58, 159.81, 164.08, 164.17, 165.38. Anal. Calcd for $C_{68}H_{88}N_2O_8$: C, 76.95; H, 8.36. Found C, 76.78; H, 8.38.

4.2.17. N,N-(1,9-Nontylene)-bis(4-hexyloxynaphthalenelidenimine) ***1e*** *(m=9, n=6).* Light yellow solids, yield 79%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.93 (t, 6H, $-CH_3$, J=6.69 Hz), 1.34−1.39 (m, 20H, $-CH_2$), 1.49−1.53 (m, 4H, $-CH_2$), 1.69−1.72 (m, 4H, $-CH_2$), 1.85−1.88 (m, 4H, $-CH_2$), 3.59 (t, 4H, $-CH_2-N{=}CH$, J=6.66 Hz), 4.10 (t, 4H, $-OCH_2$, J=6.49 Hz), 6.76 (d, 2H, Ar−H), 6.86 (s, 2H, Ar−H), 7.16 (s, 2H, Ar−H), 7.19 (d, 2H, Ar−H, J=6.80 Hz), 7.28 (d, 2H, Ar−H, J=8.38 Hz), 7.78 (d, 2H, Ar−H, J=8.64 Hz), 7.87 (d, 2H, Ar−H, J=8.84 Hz), 8.12 (d, 2H, Ar−H, J=8.61 Hz), 8.32 (s, 2H, $-N{=}CH$), 8.68 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.37, 22.94, 26.10, 27.38, 29.45, 29.51, 29.68, 31.07, 31.91, 59.22, 68.54, 106.76, 111.03, 112.44, 116.94, 120.47, 124.45, 126.44, 127.33, 128.10, 131.32, 132.13, 132.38, 137.98, 154.56, 159.79, 164.13, 164.13, 165.36. Anal. Calcd for $C_{57}H_{66}N_2O_8$: C, 75.47; H, 7.33. Found C, 75.48; H, 7.38.

4.2.18. N,N-(1,9-Nontylene)-bis(4-octyloxynaphthalenelidenimine) ***1e*** *(m=9, n=8).* Light yellow solids, yield 81%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, 6H, $-CH_3$, J=6.53 Hz), 1.31−1.39 (m, 28H, $-CH_2$), 1.48−1.53 (m, 4H, $-CH_2$), 1.69−1.72 (m, 4H, $-CH_2$), 1.85−1.88 (m, 4H, $-CH_2$), 3.59 (t, 4H, $-CH_2-N{=}CH$, J=6.69 Hz), 4.10 (t, 4H, $-OCH_2$, J=6.51 Hz), 6.76 (d, 2H, Ar−H), 6.78 (s, 2H, Ar−H), 7.17 (s, 2H, Ar−H), 7.21 (d, 2H, Ar−H, J=6.93 Hz), 7.28 (d, 2H, Ar−H, J=8.41 Hz), 7.78 (d, 2H, Ar−H, J=8.67 Hz), 7.87 (d, 2H, Ar−H, J=8.99 Hz), 8.12 (d, 2H, Ar−H, J=7.08 Hz), 8.32 (s, 2H, $-N{=}CH$), 8.68 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.44, 22.99, 26.42, 27.39, 29.49, 29.51, 29.58, 31.08, 32.15, 59.22, 68.55, 106.77, 111.03, 112.45, 116.94, 120.48, 124.46, 126.44, 127.33, 128.11, 131.33, 132.14, 132.38, 137.98, 154.57, 159.80, 164.13, 165.37. Anal. Calcd for $C_{61}H_{74}N_2O_8$: C, 76.06; H, 7.74. Found C, 75.93; H, 7.89.

4.2.19. N,N-(1,9-Nontylene)-bis(4-decanoxynaphthalenelidenimine) ***1e*** *(m=9, n=10).* Light yellow solids, yield 78%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 6H, $-CH_3$, J=6.53 Hz), 1.27−1.37 (m, 36H, $-CH_2$), 1.46−1.51 (m, 4H, $-OCH_2$), 1.67−1.70 (m, 4H, $-CH_2$), 1.82−1.86 (m, 4H, $-CH_2$), 3.57 (t, 4H, $-CH_2-N{=}CH$, J=6.64 Hz), 4.09 (t, 4H, $-OCH_2$, J=6.52 Hz), 6.73 (d, 2H, Ar−H), 6.83 (s, 2H, Ar−H), 7.15 (s, 2H, Ar−H), 7.20 (d, 2H, Ar−H, J=6.73 Hz), 7.26 (d, 2H, Ar−H, J=8.41 Hz), 7.77 (d, 2H, Ar−H, J=8.65 Hz), 7.85 (d, 2H, Ar−H, J=8.99 Hz), 8.11 (d, 2H, Ar−H, J=8.49 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.15, 22.70, 26.11, 27.08, 29.17, 29.21, 29.35, 29.38, 29.42, 29.59, 30.77, 31.92, 58.94, 68.24, 106.43, 110.72, 112.14, 116.64, 120.17, 124.13, 126.13, 127.02, 127.78, 131.02, 131.83, 132.06, 137.66, 154.23, 159.48, 163.77, 163.82, 165.06. Anal. Calcd for $C_{65}H_{82}N_2O_8$: C, 76.59; H, 8.11. Found C, 76.48; H, 8.09.

4.2.20. N,N-(1,9-Nontylene)-bis(4-dodecyloxynaphthalenelidenimine) ***1e*** *(m=9, n=12).* Light yellow solids, yield 83%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 6H, $-CH_3$, J=6.73 Hz), 1.25−1.37 (m, 46H, $-CH_2$), 1.46−1.51 (m, 4H, $-CH_2$), 1.67−1.70 (m, 4H, $-CH_2$), 1.83−1.86 (m, 4H, $-CH_2$), 3.57 (t, 4H, $-CH_2-N{=}CH$, J=6.62 Hz), 4.08 (t, 4H, $-OCH_2$, J=6.52 Hz), 6.74 (d, 2H, Ar−H), 6.84 (s, 2H, Ar−H), 7.15 (s, 2H, Ar−H), 7.20 (d, 2H, Ar−H, J=8.53 Hz), 7.26 (d, 2H, Ar−H, J=8.41 Hz), 7.76 (d, 2H, Ar−H, J=8.64 Hz), 7.85 (d, 2H, Ar−H, J=8.99 Hz), 8.10 (d, 2H, Ar−H, J=7.07 Hz), 8.31 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.17, 22.73, 26.12, 27.09, 29.18, 29.22, 29.39, 29.44, 29.62, 29.64, 29.67, 29.70, 30.77, 31.95, 58.95, 68.23, 106.41, 110.72, 112.15, 116.63, 120.18, 124.11, 126.14, 127.02, 127.77, 131.02, 131.83, 132.07, 137.66, 154.22, 159.48, 163.78, 163.82, 165.08. Anal. Calcd for $C_{69}H_{90}N_2O_8$: C, 77.06; H, 8.43. Found C, 76.93; H, 8.73.

4.2.21. N,N-(1,9-Nontylene)-bis(4-tetradecanoxynaphthalenelidenimine) ***1e*** *(m=9, n=14).* Light yellow solids, yield 81%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 6H, $-CH_3$, J=6.45 Hz), 1.25−1.37 (m, 60H, $-CH_2$), 1.49−1.52 (m, 4H, $-CH_2$), 1.67−1.70 (m, 4H, $-CH_2$), 1.82−1.87 (m, 4H, $-CH_2$), 3.57 (t, 4H, $-CH_2-N{=}CH$, J=6.43 Hz), 4.08 (t, 4H, $-OCH_2$, J=6.36 Hz), 6.74 (d, 2H, Ar−H), 6.84 (s, 2H, Ar−H), 7.15 (s, 2H, Ar−H), 7.20 (d, 2H, Ar−H, J=8.53 Hz), 7.26 (d, 2H, Ar−H, J=8.36 Hz), 7.76 (d, 2H, Ar−H, J=8.63 Hz), 7.85 (d, 2H, Ar−H, J=8.93 Hz), 8.10 (d, 2H, Ar−H, J=8.47 Hz), 8.30 (s, 2H, $-N{=}CH$), 8.66 (s, 2H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.16, 22.73, 26.11, 27.09, 29.18, 29.22, 29.40, 29.43, 29.62, 29.64, 29.70, 29.72, 30.77, 31.95, 58.95, 68.23, 106.41, 110.72, 112.15, 116.64, 120.17, 124.12, 126.14, 127.02, 127.78, 131.02, 131.83, 132.07, 137.67, 154.22, 159.48, 163.78, 163.82, 165.07. Anal. Calcd for $C_{73}H_{98}N_2O_8$: C, 77.48; H, 8.73. Found C, 77.44; H, 8.42.

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References and notes

1. Vorländer, D. *Z. Phys. Chem.* **1927**, *126*, 449−472.
2. (a) Imrie, C. T.; Henderson, P. A. *Chem. Soc. Rev.* **2007**, *36*, 2096−2124; (b) Imrie, C. T.; Henderson, P. A.; Yeap, G. Y. *Liq. Cryst.* **2009**, *36*, 755−777.
3. (a) Nishiyama, I.; Yamamoto, J.; Goodby, J. W.; Yokoyama, H. *J. Mater. Chem.* **2001**, *11*, 2690−2693; (b) Yeap, G. Y.; Hng, T. C.; Takeuchi, D.; Osakada, K.; Ahmad, W.; Mahmood, K.; Ito, M. M. *Mol. Cryst. Liq. Cryst.* **2009**, *506*, 134−149; (c) Wang, H.; Shao, R.; Zhu, C.; Bai, B.; Gong, C.; Zhang, P.; Li, F.; Li, M.; Clark, N.

A. *Liq. Cryst.* **2008**, *35*, 967–974; (d) Bai, B.; Wang, H.; Zhang, P.; Qu, S.; Li, F.; Yu, Z.; Long, B.; Li, M. *Liq. Cryst.* **2008**, *35*, 793–798.

4. Nishiyama, I.; Yamamoto, J.; Goodby, J. W.; Yokoyama, H. *Liq. Cryst.* **2004**, *31*, 1495–1502.
5. (a) Białecka-Florjanczyk, E.; Sledzinska, I.; Górecka, E. *Liq. Cryst.* **2012**, *39*, 1216–1221; (b) Campo, A. D.; Meyer, A.; Perez, E.; Bello, A. *Liq. Cryst.* **2004**, *31*, 109–118.
6. (a) Photinoes, D. J.; Samulski, E. T.; Torlumi, H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1875–1883; (b) Tschierske, G.; Koehler, H.; Kleinpeter, E.; Zaschke, H. In Proceedings of the 18th Freiburger Arbeitstagung Fluessigkristalle, 1989, pp 1–7.
7. (a) Pivnenko, M. N.; Lehmann, P.; Komitov, L.; Coles, H. J. *Liq. Cryst.* **2005**, *32*, 173–181; (b) Olsson, N.; Helgee, B.; Andersson, G.; Komitov, L. *Liq. Cryst.* **2005**, *32*, 1139–1150.
8. (a) Białecka-Florjanczyk, E.; Sledzinska, I.; Gorecka, E.; Przedmojski, J. *Liq. Cryst.* **2008**, *35*, 401–406; (b) Senthil, S.; Rameshbabu, K.; Wu, S. L. *J. Mol. Struct.* **2006**, *783*, 215–220; (c) Duer, M. J.; Roper, C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3034–3041.
9. Centore, R.; Roviello, A.; Tuzi, A.; Sirigu, A. *Liq. Cryst.* **2006**, *33*, 929–933.
10. (a) Niori, T.; Adachi, S.; Watanabe, J. *Liq. Cryst.* **1995**, *19*, 139–148; (b) Prasad, S. K.; Sandhya, K. L.; Nair, G. G.; Hiremath, U. S.; Yelamaggad, C. V. *J. Appl. Phys.* **2002**, *92*, 838–841; (c) Date, R. W.; Luckhurst, G. R.; Shuman, M.; Seddon, J. M. *J. Phys. II France* **1995**, *5*, 587–606; (d) Weissflog, W.; Lischka, C.; Diele, S.; Wirth, I.; Pelzl, G. *Liq. Cryst.* **2000**, *27*, 43–50.
11. Hori, K.; Iimuro, M.; Nakao, A.; Toriumi, H. *J. Mol. Struct.* **2004**, *699*, 23–29.
12. (a) Yelamaggad, C. V.; Shanker, G. *Tetrahedron* **2008**, *64*, 3760–3771; (b) Nishiyama, I. ,; Yamamoto, J.; Goodby, J. W.; Yokoyama, H. *J. Mater. Chem.* **2001**, *12*, 1709–1716; (c) Yelamaggad, C. V.; Shanker, G. *Liq. Cryst.* **2007**, *34*, 1045–1057.
13. (a) Kosata, B.; Tamba, G. M.; Baumeister, U.; Pelz, K.; Diele, S.; Pelzl, G.; Galli, G.; Samaritani, S.; Agina, E. V.; Boiko, N. I.; Shibaev, V. P.; Weissflog, W. *Chem. Mater.* **2006**, *18*, 691–701; (b) Umadevi, S.; Sadashiva, B. K.; Murthy, H. N. S.; Raghunathan, V. A. *Soft Matter* **2006**, *2*, 210–214; (c) Kumar, S. *Liq. Cryst.* **2005**, *32*, 1089–1113.
14. Varia, M. C.; Kumar, S.; Prajapati, A. K. *Liq. Cryst.* **2012**, *39*, 933–942.
15. Liao, C. C.; Wang, C. S.; Shen, H. S.; Lai, C. K. *Tetrahedron* **2008**, *64*, 7977–7985.
16. Srivastava, R. M.; Neves Filho, R. A. W.; Schneider, R.; Vieira, A. A.; Gallardo, H. *Liq. Cryst.* **2008**, *35*, 737–742.
17. (a) Yelamaggad, C. V.; Tamilenthi, V. P. *Tetrahedron* **2009**, *65*, 6403–6409; (b) Yelamaggad, C. V.; Shashikala, I. S.; Rao, D. S. S.; Nair, G. G.; Prasad, S. K. *J. Mater. Chem.* **2006**, *16*, 4099–4102; (c) Achten, R.; Koudijs, A.; Karczmarzyk, Z.; Marcelis, A. T. M.; Sudholter, E. J. R. *Liq. Cryst.* **2004**, *31*, 215–227; (d) Yelamaggad, C. V.; Mathews, M.; Hiremath, U. S.; Nair, G. G.; Rao, D. S. S.; Prasad, S. K. *Liq. Cryst.* **2003**, *30*, 899–907.
18. (a) Yeap, G. Y.; Hng, T. C.; Yeap, S. Y.; Gorecka, E.; Ito, M. M.; Ueno, K.; Okamoto, K.; Mahmood, W. A. K.; Imrie, C. T. *Liq. Cryst.* **2009**, *36*, 1431–1441; (b) Imrie, C. T. *Liq. Cryst.* **2006**, *33*, 1449–1454; (c) Sepelj, M.; Lesac, A.; Baumeister, U.; Diele, S.; Nguyen, H. L.; Bruce, D. W. *J. Mater. Chem.* **2007**, *17*, 1154–1165.