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Key words: salicylaldazines, salicylaldimines, mesogens, smectic, nematic

The π - π interactions enhanced in salicylaldimines and salicylaldazines

Hsiu–Ming Kuo, Yu–Te Hsu, Yi–Wen Wang, Gene–Hsiang Lee,[†] Chung K. Lai* Department of Chemistry, National Central University, Chung–Li, Taiwan, ROC [†]Instrumentation Center, National Taiwan University, Taipei 10660, Taiwan, ROC

Abstract. Four new series of salicylaldazines **1** and salicylaldimines **2–4** were prepared, characterized and their mesomorphic properties were studied. The structures of all compounds were identified and confirmed by spectroscopic techniques such as ¹H, ¹³C–NMR, MS and elemental analysis. Three single crystallographic structures of compounds **1a** (n = 3, 6) and **2** (n = 3) were determined by X–ray analysis in order to correlate the molecular structures with the formation of mesophases. Crystallographic data indicated that the better mesomorphic properties might be controlled by CH– π , π – π or/and H–bonds in such system. Except for crystalline compounds **4**, all other compounds **1–3** showed mesomorphic behavior of nematic, smectic A or/and smectic C phases, which were characterized by differential scanning calorimetry, optical polarizing microscope and X–ray diffraction experiments. All compounds **1–4** showed yellow–green photoluminescence in THF occurred at 519–521 nm.

^{*} Corresponding author. Tel.: +886 03 4259207; fax: +886 03 4277972.

E-mail address: cklai@cc.ncu.edu.tw (C.K.Lai)

1.0 Introduction

The demeric liquid crystals have been extensively investigated since the first example¹ reported on 1927. In general, the structures of dimeric LCs constituted two mesogenic moieties linked via a flexible spacer or a rigid core. Mesogenic structures linked by a flexible spacer such as alkyls (-CH₂-), esters (-COOCH₂OOC-) and ethers (-OCH₂O-) are often called twin liquid crystals or liquid crystal dimers. These dimers were particularly of appealing because of their unique thermal behavior and structural features as model compounds similar to polymeric liquid crystals. These compounds are also known as bimesogens. The molecular conformations and mesomorphic behavior were quite differential from classical (or monomeric) mesogens. On the other hand, their mesomorphic properties were significantly influenced by the spacer length and also the linking group. This type of molecules is often made by linking either two identical or non-identifical moieties through a flexible central spacer. Numerous examples² of DLCs were reported. Three types of layered smectic phases; monolayer, interdigitated or intercalated conformations were proposed depending on their spacing and/or molecular length. Shape–effect³ caused by odd or even carbon atoms incorporated in the spacer was often observed. Among them, salicylaldehydes are probably one of the core structures utilized the most to generate the mesogenic materials, including symmetric and asymmetric structures during the past decades. A variety of novel metallomesogens⁴ derived from salicylaldehydes or their Schiff bases of salicyladimines were reported. Numerous salicyladimine-based dimeric LCs⁵ were prepared, and most of mesogenic dimeric LCs have a flexible central spacer. However, known examples⁶ of similar mesogenic structures with a more rigid spacer were relatively rare.

In contrast, salicylaldazines ($R_1R_2C=N-N=CR_1R_2$), similar to salicylaldimines ($R_1R_2C=N-R-N=C R_1R_2$) can be prepared by the condensation reactions⁷ of salicylaldes with hydrazine. It has been used as precursors⁸⁻⁹ to synthesize hydrazones ($R_1R_2C-NNH_2$)¹⁰, diazo ($R_1R_2C=N_2$) and heterocyclic compounds¹¹. In alicyclic chemistry, azines are compounds resulting from the reactions of two identical or different carbonyl compounds with hydrazine.

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Azines that are N–N linked diimines are 2,3–diaza analogs of 1,3–butadiene. An azine moiety formed by two imine bonds can be considered as polar acceptor oriented in opposite directions.¹² Azines are two conjugated double-bond structure, similar to 1,3–dienes, 1,2–diimines, 1,2–diones. However, extensive X–ray analyses about the N–N and Ar–C bonds showed no evidence¹³ of conjugation, and in fact the azine unit is a "conjugation stopper". Asymmetric azines appended with donor and acceptor moieties incorporated on the terminal backbone showed novel organic non linear optical (NLO) materials.¹⁴ A few similar examples¹⁵ of mesogenic azines (such as **Ia–b**) have been reported and studied.



In order to understand the core effect on the formation of mesophases in azines and more rigid diimines, in this work, we describe the synthesis, characterization, and the mesomorphic properties of four series of compounds **1–4** derived from salicylaldehydes. An extended π -conjugated structure by incorporation of phenylene or biphenylene was also studied in compounds **2–4**. All compounds **1–3** were mesogenic, giving nematic, smectic A or smectic C phases, whereas, compounds **4** were crystals. Three single crystals were investigated to understand the possible correlation of mesomoropisms and structures. The structural analysis appeared that a better core planarity was formed by intramolecular H–bonds in this type of compounds. On the other hand, a good layered arrangements enhanced by π – π intermolecular interactions also facilitated the formation of meosophases. Most of known mesogenic dimeric LCs have a flexible central spacer. However, examples of similar mesogenic structures with a more rigid spacer were relatively rare.

2.0 Results and Discussion

2.1 Synthesis and characterization

The synthetic procedures for all the compounds are summarized in scheme 1. 4–Alkoxysalicylaldehyde was alkylated by controlling the basicity and equivalent of alkyl bromides. The compounds **1–4** were carried out by double imination of alkylated salicylaldehydes and diamines with EtOH/THF as solvents. The compounds **1–4** were isolated as yellow to orange powder, depending on the spacers and yields were in the range 33–78%. Most derivatives were characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis and mass spectrometry. However, for some derivatives with a poor solubility in organic solvents to perform NMR spectroscopy, mass spectrometry and elemental analysis data were obtained. On ¹H NMR spectra, a characteristic broad peak often appeared at δ 6.53–8.56 and 11.11–11.71 ppm assigned for imine–CHN and phenolic–OH was observed for compounds **1a**. In contrast, this phenolic–OH was slightly shifted to δ 13.81 ppm. These characteristic peaks were also slightly shifted to upfield, as summarized in Table 1.

Table 1. The characteristic	chemical peaks ^a on	¹ H–NMR spectroscop	pes for compound	ds 1–4.
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Compds	1a	1b	2	3	4
-C=NH	8.53-8.56	13.81	8.53-8.54	8.87-8.90	8.94-8.97
–OH (phenolic)	11.11–11.71	_	_	9.92–9.99	9.78–9.85
–OH (phenolic)	(-) 7	-	13.64–13.70	14.51	14.40–14.44

^a: **1b** measured in DMSO–d₆ and **1a**, **2–4** measured in CDCl₃, unit (δ) in ppm.



Scheme 1. Reactions and reagents: (a) RBr (1.1 eq.), KHCO₃ (1.5 eq.), KI, refluxed in acetone, 24 h, 41%; (b) I_2 (cat.), hydrazine monohydrate, p-phenylenediamine, 4,4'-diaminobiphenyl-3,3'-diol, or 3,3'-diaminobiphenyl-4,4'-diol, stirred at rt.

2.2 Single crystals and molecular structures of compounds 1a (n = 3, 6) and 2 (n = 3)

In order to understand the possible correlation between the molecular arrangements and their mesomorphic behavior, three single crystals of compound **1a** (n = 3, 6) and **2** (n = 3) suitable for crystallographic analysis were obtained by slow diffusion from THF/EtOH at room temperature and their structures resolved. Figure 1 shows their molecular structures. Table 2 lists their crystallographic and structural refinement data for the crystals. They crystallize in a monoclinic space P2(1)/c for compound **1a** (n = 3) and a triclinic space group P-1 for compounds **1a** (n = 6) and **2** (n = 3). All three crystals were considered as slightly linear–shaped with a molecular length of 22.38 Å (C10–10'), 28.78 Å (C20-C26) and 24.12 Å (C26-C26'), required for the formation of nematic or smectic phases.



Fig. 1 Three ORTEP plots and molecular lengths for crystals 1a (n = 3), 1a (n = 6) and 2 (n = 3). The thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

<u>_</u>			,
Compd.	1a (n = 3)	1a $(n = 6)$	2 (n = 3)
Empirical formula	$C_{10}H_{12}NO_2$	$C_{26}H_{36}N_2O_4$	$C_{26}H_{28}N_2O_4$
Formula weight	178.21	440.57	432.50
Temperature (K)	296(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	P-1	P-1
a(Å)	8.8100(5)	7.7266(2)	6.3422(7)
b(Å)	10.8004(6)	11.0341(3)	7.0827(8)
c(Å)	9.9027(5)	15.2879(5)	24.585(3)
α(°)	90	102.594(2)	83.588(2)
β(°)	98.807(3)	101.332(2)	82.952(2)
γ(°)	90	100.517(2)	88.981(2)
Volume ($Å^3$), Z	931.15(9), 4	1212.14(6), 2	1089.2(2), 2
Density (calculated, Mg/m ³)	1.271	1.207	1.319
Crystal size (mm ³)	0.4x0.1875x0.05	0.60x0.18x0.12	0.38x0.36x0.05
θ range for data collection(°)	2.34-28.46	1.41-27.50	0.84-25.00
Reflections collected	8517	20213	10296
Final R1, wR2	0.0415, 0.1023	0.0534, 0.1312	0.0860, 0.2146

Table 2 Crystal data and structure refinements for 1a (n = 3, 6) and 2 (n = 3).

As expected, intramolecular H–bonds were all observed in the crystal lattices for all three crystals shown in Figure 2. Each crystal has two intramolecular H–bonds; they are relatively strong and their bond lengths ranged from d = 1.848-1.936 Å, summarized in Table 3.

However, there was no intermolecular H–bond observed in all three crystals. A dihedral angle of $ca \sim 0^{\circ}$ and $\sim 5.74^{\circ}$ between the two phenyl rings was observed for in crystals **1a** (n = 3 and n = 6), respectively. In contrast, a larger dihedral angle of $\sim 47.8^{\circ}$ in crystal **2** (n = 3) was observed. A better planar structure and an extended molecular shape are often responsible for a good packing in solid and/or liquid crystal state. In addition, intermolecular interactions of σ – π or π – π interactions were also observed in these crystals, and their distances ranged from 2.65–4.15 Å, listed in Table 4. These intermolecular forces apparently facilitated the formation of mesophases in this type of compounds. All molecules arranged in a style of layered structure. The molecular arrangements of three crystals in crystal lattices are shown in Figure 3.



Fig. 2 Intramolecular H–bonds and intermolecular interactions (π – π and/or CH– π) observed in compounds **1a** (n = 3, top plot), **1a** (n = 6, middle plot) and **2** (n = 3, bottom plot). Bond distances are in red figures (Å).

Table 3. Intramolecular H-bonds observed in Ta $(n = 3, 6)$ and $Z (n = 3)$.					
no. H–bonds $(O - H N)$	bond distance/Å	angles/°			
(0-111)					
2	N1 - H2A = 1.94	$\angle N1 - H2A - O2 = 144.36$			
2	N1-H1 = 1.88	$\angle N1$ -H1-O1 = 146.18			
	N2-H2 = 1.91	$\angle N1 - H2 - O2 = 146.76$			
2	N2-H3A = 1.85	$\angle N2 - H3A - O3 = 147.56$			
	noiecular H–bonds no. H–bonds (O–HN) 2 2 2	nolecular H-bonds observed in 1a (n = 3, 6) a no. H-bonds bond distance/Å $(O-HN)$ 0 2 N1-H2A = 1.94 2 N1-H1 = 1.88 N2-H2 = 1.91 N2-H3A = 1.85			

Table 3. Intramolecular H-bonds observed in **1a** (n = 3, 6) and **2** (n = 3).

Table 4. Intermolecular interactions observed in 1a (n = 3, 6) and 2 (n = 3).

Compds.	no. of $\sigma - \pi$ or $\pi - \pi$ interactions	distance ^a /Å	angles/°
1 (n = 3)	4	ring-H2A = 2.87	∠ring–H2A–C9 =145.78
1 (n = 6)	2 (ArAr)	ring-ring = 4.15	∠ring-H1A-C1 =128.29
2 (n = 3)	2 (Ar–H…Ar)	ring-H1A= 2.89	∠ring–H1A–C1 =128.29
	2 (Ar–H…Ar)	ring-H20= 2.92	\angle ring-H20-C20 =128.29
	2 (Ar–H…Ar)	ring-H23= 2.65	\angle ring-H23-C23 =133.80

^a: measured from the center of ring to the atom.



Fig. 3 Layer structures of compound **1a** (n = 3, left), **1a** (n = 6, middle) and **2** (n = 3, right) along a axis.

2.3 Mesomorphic properties of compound 1-4

The thermal behavior of compounds **1–4** was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperatures and

enthalpies of the compounds are listed in Table 5. Except for compounds **4**, all other compounds **1–3** are mesogenic. All compounds **1a** exhibited kinetically stable enantiotropic behavior, giving smectic C phase at lower temperatures or/and nematic at higher temperatures. Both melting and clearing temperatures decreased with carbon lengths of alkoxy chains. The melting temperatures were ranged between $T_{melting} = 173.7$ (n = 3) – 107.8 °C (n = 10), while clearing temperatures were ranged between $T_{cl} = 183.7$ °C (n = 3) – 147.6 °C (n = 16). On the other hands, the temperature ranges of mesophases remained at $\Delta T_M = 23.2$ (n = 3) – 68.8 °C (n = 8) during the cooling process. Under optical microscope, compounds **1a** exhibited fan–shaped or focal–conics textures at lower temperatures and Schlieren textures at higher temperatures (Fig. 4). These optical textures were characteristic of a SmC phase or N phases, expected for the rod–like molecules. Under optical microscope, the texture of SmC phase showed no homeotropic domains.

In order to understand the effect of core planarity on the formation of the mesophases, two compounds **1b** (n = 3, 6) incorporated with a methyl group bonded to the imine moiety (-C=NH) were prepared and their mesomorphic behavior compared with compounds **1a**. The geometry of methyl group is relatively bulkier tetrahedron. The bulkier methyl moiety, when close to the core center, will reduce the molecular interactions between the neighboring layers. Thus, a lower clearing temperature was often observed. Compounds **1b** (n = 3, 12) exhibited SmC/SmA or N phase, however, compounds **1a** (n = 3, 12) formed SmC or N phase. Interestingly, the data indicated that the clearing temperatures of both derivative **1b** (n = 3, 6) were slightly higher than those of compounds **1a** (n = 3, 12) by *ca*. $\Delta T = 31.3$ (n = 3) and 13.1 °C (n = 12), respectively. On the other hand, the temperature of mesophases for derivative **1b** (n = 3) was much wider than that of derivative **1a** (n = 3), $\Delta T_{meso} = 103.6 > 23.1$ °C. In contrast, other derivative **1b** (n = 12) had a narrower temperature range than that of **1a** (n = 12), $\Delta T_{meso} = 45.0 < 50.2$ °C. Apparently, the derivative **1b** (n = 3) has a better aspect ratio (d/l) of molecules, required to be improved mesogens. A tetrahedral methyl moiety, not near by the core might exert little effect on the formation of mesophases.

When a phenylene group in compounds **2** was incorporated as a core group, the mesomorphic behavior was apparently altered. The phenylene group was structurally considered as a more rigid and more planar moiety, and potential π - π interactions might be better induced. Indeed, the mesomorphic properties were greatly improved. Both melting and clearing temperatures of compounds **2** was raised; the clearing temperatures were higher than those of compounds **1a** by $\Delta T = 103.5$ (n = 3) > 99.6 (n = 8) > 87.3 °C (n = 14). In contrast, the melting temperatures of compounds **2** were higher by $\Delta T_{melting} = 9.10$ (n = 8) > 4.30 (n = 3) > 1.00 (n = 14) °C, thus giving a much wider temperature range of mesophases by $\Delta T_{meso} = 136.1$ (n = 3) -184.9 °C (n = 8). The stronger σ - π or π - π interactions between the neighboring phenylene groups within the layers might be attributed to the improved mesophases. This is quite consistent with the single crystalline crystallographic data, discussed later. Optical textures observed under POM also confirmed the mesophases.

			AC	CE	PTED MA	NUS	CRIPT			
Table	5. Phase	transi	tions ^a and enth	alpies	s of compounds	s 1-4.				
1a:	n = 3					C -	173.7 (50.6)	N	183.7 (0.72)	
,						Cr	159.2 (53.1)	N	182.4 (0.87)	1
	6			<u> </u>	130.9 (38.5)	SmC	160.1 (2.15)	N	175.0 (1.82)	
	0			Cr	112.2 (36.6)	Sinc	157.0 (1.88)	IN 1	174.3 (1.64)	
	8	Cr.			111.6 (43.2)	SmC	169.1 (9.09)	N	169.2 ^b	
	U	01	93.1 (6.27)	Cr ₂	98.0 (36.4)	onio	165.9 (7.35)		166.8 (2.03)	•
	10	Cr₄	51.8 (1.74)	Cr ₂	73.4 (3.28)	Cra	107.8 (38.8)	SmC	165.4 (10.2)	
	10	0.1	45.3 (5.88)			0.3	99.4 (39.8)	onio	161.0 (9.01)	•
	12			Cr₄	58.4 (10.3)	Cr ₂	111.9 (50.6)	SmC	158.9 (12.6)	
				0.1	61.4 (9.08)	0.2	107.4 (51.8)	onio	157.6 (11.9)	Y
	14	Cr.			75.1 (5.20)	Cr ₂	112.6 (55.6)	SmC	149.4 (11.8)	Ϊ.
	14	01	66.7 (2.05)	Cr ₂	82.1 (4.24)	0.3	107.4 (55.4)	onio	148.0 (10.4)	•
	16			Cr			116.3 (72.9)	SmC	147.6 (14.8)	T
				CI	95.8 (3.37)	Cr ₂	112.2 (72.4)		145.9 (14.6)	
1b; n	= 3					Cr	111.9 (50.6)	N	215.0 ^b	
						•	107.4 (51.8)		211.0 (0.80)	•
	12			Cr₁	138.4 (43.2)	SmC	163.2 (0.59)	SmA	172.0 (11.6)	Т
				- 1	125.2 (43.8)		162.8 (0.35)		170.2 (11.1)	
2∙ r	1 = 3					Cr	178.0 (28.2)	SmA -	287.2 (1.19)	
_,.	0					0.	133.7 (23.5)	01111	269.8 (0.53)	•
	8			Cr	120.7 (31.3)	SmC	254.8 (2.51)	SmA -	268.8 (5.95)	ı.
	U			0.	76.0 (27.1)	00	250.9 ^b	•••••	260.9 (5.69)	-
	14			Cr₁	103.9 (39.7)	Cr ₂	113.6 (52.9)	SmC	236.7 (12.7)	T
				- 1	91.5 (41.7)		98.5 (51.5)	••	234.0 (12.4)	
3: n	= 3					Cr –	343.6	N	349.8	Ы
-,	-									u
	8					Cr –	332.5	SmA ·	348.1	۱ _d
						1				-
	14					Cr –	310.9	SmA	323.9	l _d
										-
4; r	n = 3				XY			Cr	300.4 (74.9)	l _d
,										
	8							Cr -	297.4 (98.4)	l _d
									004 0 (00 O)	
	14							Cr	284.2 (96.9) 	I_{d}

^a: n is the carbon number of alkoxy groups. Cr₁, Cr₂, Cr₃ = crystal, SmC = smectic C, SmA = smectic A, nematic = N, I = isotropic phase and I_d = isotropic phase with a decomposition at a scan rate of 10 ^oCmin⁻¹.
 ^b: observed by POM.



Fig. 4 Optical textures observed. SmC phase at 160 °C (top left) by **1a** (n = 8), SmC phase at 154°C (top right) by **1a** (n = 10), N phase at 306 °C (bottom left) by **2** (n = 3) and SmA phase at 262 °C (bottom right) by **2** (n = 8).



Fig. 5 Bar graphs showing the phase behavior of compounds **1–4**. All temperatures were taken from cooling process.

To further test the structural effect on the formation of the mesophases, compounds 3 and 4 were also prepared and studied. A biphenylene with two hydroxyl groups substituted at 3, 3'- and 4, 4'-position was incorporated to generate the compounds 3 and 4, respectively. H-bonds might be also induced between the neighboring layers if all molecules were correctly supplementary. All compounds 3 were truly mesogenic, whereas, all compounds 4 were not mesogenic. The results were in fact not surprising. Compounds 3 were more linear-like and more rod in shapes, while compounds 4 were more lath-like or more ellipsoid (See Fig. 6). Both compounds 3-4 were not all thermally stable, and partial decompositions on heating above their clearing temperatures were observed. The results showed that all compounds 3 (n = 3, 8, 14) formed N or SmA phase, however, all compounds 4 exhibited crystalline phases. All clearing temperatures of compounds **3** were ranged in 323.9–349.8 °C, all much higher than those of compound **1a** and **2** due to their more rigid structures and/or larger molecules. The temperature ranges of mesophases were relatively short, $\Delta T = 6.2$ (n = 3) < 13.0 (n = 14) < 15.6 °C (n = 8) on the heating process. Compounds 4 were all crystalline solids, and a transition temperature of crystal-to-isotropic states at T = 300.4 (n = 3) > 297.4 (n = 8) > 284.2 °C (n = 14) were only observed.



Fig. 6 Schematic representation of molecular shaped by compounds 3 and 4.

The thermal stability of compounds **1a**, and **2–4** (n = 8) was also performed by thermogravimetric analyses (TGA) under nitrogen atmosphere, shown in Fig. 7. All four compounds showed relatively good thermal stability at temperature below ca. 295.0 °C, with a relative thermal stability of **1a** > **2** > **3~ 4**. The decomposition temperatures for a 5% weight loss were listed in Table 6. Surprisingly, the decomposition temperature of **1a** and **2** was slightly higher than that of **3–4** by *ca*. $\Delta T = 30$ °C, which is not consistent with the DSC data of these two compounds. Compound **1a** and **2** has a flexible alkyl spacer, in contrast, compounds **3–4** have a more rigid phenyl or biphenyl spacer. The clearing temperature of compounds was decreasing at $T_{cl} = 348.1$ (**3**, n = 8) > 297.4 (**4**, n = 8) > 268.8 (**2**, n = 8) > 169.2 (**1a**, n = 8) °C.



Fig. 7 The TGA thermographs of compounds **1a** and **2–4** (all n = 8) under nitrogen gas at a heating rate of 10.0 °Cmin⁻¹

Compds	T_{dec} (°C)
1a (n = 8)	326.3
2 (n = 8)	325.1
3 (n = 8)	295.0
4 (n = 8)	295.0

Table 6. The decomposition temperatures^a of compounds 1–4 by TGA analysis.

^a: Temperatures taken with a 5% weight loss.

2.4 Powder X-ray diffraction of compounds 1-2

Variable–temperature powder X–ray diffraction experiments were conducted to confirm the structure of the mesophases of compounds **1a** (n = 12) and **2** (n = 8). The X–ray diffraction plots of both compounds are present in Figure 8. It displayed a typical diffraction pattern with

one strong peak at low angle region followed by a weak peak and a broad peak at wider angle. These are characteristic of layered arrangements of SmC phases with d–spacing ratio of 1 and 1/2, corresponding to Miller indices; 100 and 200, respectively. For example, a diffraction pattern at 140 °C with d–spacing at 34.23 Å, 17.09 Å and a broad diffused peak (~ 4.62 Å) at wide–angle region was observed for compound **1a** (n = 12) and this diffraction pattern corresponded to a SmC phase. The d–spacing of 34.23 Å was slightly smaller than 43.06 Å, which was obtained from calculated molecular length by MM2 model. This might indicate that the molecules were tilted and/or the side chains were interdigitated. The broad peak observed at about 4.62 Å was assigned to the molten side chains. Similarly, the two powder X–ray diffractions of compounds **2** (n = 8) at 140 °C and 257 °C was shown in Figure 8. In smectic C phase at 140 °C, it showed one strong peak at 32.85 Å and a much weaker peak at 16.35 Å. These two diffraction peaks corresponded to Miller indices 100 and 200. However, in smectic A phase at higher temperature of 257 °C, it showed only one strong peak at 37.30 Å. The diffraction intensity at SmA phase was much weaker than that at SmC phase. Two halo peaks were also observed at ~ 4.54 and 4.81 Å.



Fig. 8 The powder X–ray diffraction plots of SmC by compound **1a** (n = 12, top plot) at 140 °C SmC by **2** (n = 8, middle plot) at 140 °C and SmA by **2** (n = 8, bottom plot) at 257 °C.

2.5 Optical properties

The UV-vis absorption and PL spectra of the compounds 1-4 (all n = 8) measured in THF solution at room temperature are presented in Figure 9. The λ_{max} peaks of UV–vis absorption and the λ_{em} of PL spectra were listed in Table 7. The two strong absorption λ_{max} peaks of compounds 1-4 occurred at ca. 283-305 and 352-390 nm, which were attributed to $n-\pi^*$ and $\pi-\pi^*$ transitions arising from salicylaldehyde moiety. The absorption peaks increased with an extended core conjugation introduced from compound 1 to compound 3. Compound **3** has a largest absorption of 390 nm due to its biphenyl core. In contrast, the absorptions of compound 4 decreased to 352 due to its meta-position. The PL spectra of all compounds 1–4 were quite similar, showing one intense and broad peak occurred at λ_{em} = 519–521 nm. Interestingly, an extended conjugated length in compounds 2–3 showed no apparent red-shift emission compared to compounds 1a. This was probably due to the poor coplanarity of the molecules in the crystal packing, reducing the effect of aggregation induced red-shift. In fact, this result was quite consistent with single crystallographic data obtained in crystal 2 (n = 3); a twisting angle of $\sim 47.8^{\circ}$ between the central phenyl ring and salicylaldimine was observed. A relatively weak emission was obtained for compounds 1-4 which be attributed to a possible proton transfer¹⁶ between the imine moiety and neighboring phenolic-OH.



Fig. 9 Absorption (top) and PL (bottom) spectra of compounds **1–4** measured in THF at room temperature.

Table 7. The UV–vis absorptions and PL–emissions^a of compounds 1–4.

Compd.	absorption/nn	emission λ_{max}/nm
1a (n = 8)	305, 370	520.9
2 (n = 8)	284, 380	519.8
3 (n = 8)	283, 390	520.8
4 (n = 8)	288, 352	518.9

^a: all measured in THF solution $(1.0 \times 10^{-5} \text{ M})$ at rt.

3. Conclusions

Four new series of salicylaldazines **1** and salicylaldimines **2–4** were prepared, characterized and their mesomorphic properties studied. All compounds **1–3** showed mesomorphic behavior of nematic, smectic A or/and smectic C phases and exhibited relatively good thermal stability on TGA. Crystallographic data indicated that the mesomorphic

properties were greatly improved by CH– π , π – π or/and H–bonds in such system. All compounds 1–4 showed yellow–green photoluminescence in THF occurred at 519–521 nm. An extended core π –conjugated structure in compounds 2–4 showed no red–shift photoluminescence due to their non–coplanar core planes. Their possible metallomesogens will be explored in the future.

4.0 Experimental Section

4.1 General materials and methods

All chemicals and solvents were reagent grade from Aldrich Chemical Co., and solvents were dried by standard techniques. ¹H and ¹³C NMR spectra were measured on a Bruker DRS–300. 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. Elemental analyses were performed on a Heraeus CHN–O–Rapid elemental analyzer. The powder diffraction data were collected from the Wiggler–A beam line of the National Synchrotron Radiation Research Center (NSRRC) with a wavelength of 1.3223 Å. 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 3, 3'-Dinitrobiphenyl-4, 4'-diol

To a solution of biphenyl-4,4'-diol (9.3 g, 0.05 mol) dissolved in 70 mL of dichloromethane, 70% HNO₃ (9.9 g, 0.11 mol) was slowly added. The mixture was kept at 0 °C and stirred for 3 h. The solids were filtered, and washed several time with saturated aqueous solution of NaHCO₃. The products isolated as pale yellow solids was obtained after recrystallization from acetone. Yield 53%. ¹H NMR (300 MHz, DMSO–d₆): δ 7.20 (d, *J* = 4.4 Hz, Ar–H, 2H), 7.87 (d, *J* = 4.3 Hz, Ar–H, 2H), 8.15 (d, *J* = 1.2 Hz, Ar–H, 2H), 11.12 (s, Ar–OH, 2H). ¹³C NMR

(75 MHz, DMSO-d₆): δ 119.82, 122.59, 129.29, 132.94, 137.51, 151.45.

4.3 3, 3'-Diaminobiphenyl-4, 4'-diol

A solution of 3, 3'-dinitrobiphenyl-4,4'-diol (3.0 g, 11 mmol), hydrazine monohydrate (9.0 mL, 0.18 mol) and Pd/C (0.3 g) dissolved in 25 mL of absolute ethanol was stirred for 4 h. The crude products were filtered. The solids were dissolved in hot DMF and then was filtered through fresh Celite. The filtrate was poured into cold water and the precipitates were filtered. The product isolated as gray powders was obtained after recrystallization from acetone. Yield 85%. ¹H NMR (300 MHz, DMSO–d₆): δ 4.46 (bs, –NH₂, 4H), 6.52 (d, *J* = 4.05 Hz, Ar–H, 2H), 6.63 (d, *J* = 4.05 Hz, Ar–H, 2H), 6.74 (s, Ar–H, 2H), 8.88 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, DMSO–d₆): δ 112.36, 114.18, 114.51, 132.82, 136.53, 142.90.

4.4 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-propoxy phenol) 1a (n = 3)

A solution of 2-hydroxy-4-propoxybenzaldehyde (1.0 g, 5.6 mmol), hydrazine dihydrochloride (1.14 g, 11 mmol), catalytic amount of solids I₂ disolved in 30 mL of dry DMSO was stirred for 30 mins. The solution was then poured into ice water then the crude products were filtered. The light brown solid was passed through a short column of silica gel. The products isolated as pale yellow solids was obtained after crystallization from THF/Ethanol. Yield: 51%. ¹H NMR (300 MHz, CDCl₃): δ 1.02 (t, *J* = 7.5 Hz, –CH₃, 6H), 1.76–1.83 (m, –CH₂, 4H), 3.93 (t, *J* = 6.3 Hz, –OCH₂, 4H), 6.48 (d, *J* = 1.65 Hz, Ar–H, 2H), 6.51 (s, Ar–H, 2H), 7.20 (d, *J* = 4.05 Hz, Ar–H, 2H), 8.55 (s, –CHN, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 10.44, 22.38, 69.74, 101.62, 108.03, 110.74, 133.51, 161.79, 162.55, 163.61. Anal. Calcd. for C₂₀H₂₄N₂O₄: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.21; H, 6.83; N, 7.83. MS (LRFAB): M⁺ (m/z) = 356.34.

4.4.1 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-hexoxy phenol) 1a (n = 6)

Pale yellow solids, yield 63%. ¹H NMR (300 MHz, CDCl₃): δ 0.91 (t, *J* = 4.2 Hz, -CH₃, 6H), 1.29–1.48 (m, -CH₂, 12H), 1.71–1.80 (m, -CH₂, 4H), 3.96 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.47 (d, J = 3 Hz, Ar–H, 2H), 6.49 (s, Ar–H, 2H), 7.17 (d, J = 8.6 Hz, Ar–H, 2H), 8.53 (s, –CHN, 2H) , 11.36 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃)): δ 14.00, 22.56, 25.62, 29.00, 31.51, 68.26, 101.61, 107.95, 110.80, 133.43, 161.73, 162.58, 163.51. MS (LRFAB): M⁺ (m/z) = 440.42. Anal. Calcd. for C₂₆H₃₆N₂O₄: C, 70.88; H, 8.24; N, 6.36. Found: C, 70.93; H, 8.26; N, 6.27.

4.4.2 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-octyloxy phenol) 1a (n = 8)

Pale yellow solids, yield 59%. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, -CH₃, 6H), 1.27–1.43 (m, -CH₂, 20H), 1.74–1.79 (m, -CH₂, 4H), 3.96 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.47 (m, Hz, Ar–H, 2H), 6.50 (s, Ar–H, 2H), 7.20 (d, *J* = 7.8 Hz, Ar–H, 2H), 8.55 (s, -CHN, 2H), 11.11 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃): 14.08, 22.63, 25.96, 29.04, 29.20, 29.30, 31.78, 68.32, 101.64, 108.08, 110.71, 133.53, 161.83, 162.51, 163.68. MS (LRFAB): M⁺ (m/z) = 496.56. Anal. Calcd. for C₃₀H₄₄N₂O₄: C, 72.55; H, 8.93; N, 5.64. Found: C, 72.18; H, 8.92; N, 5.54.

4.4.3 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-decyloxy phenol) 1a (n = 10)

Pale yellow solids, yield 66%. ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, *J* = 6 Hz, -CH₃, 6H), 1.26–1.43 (m, -CH₂, 28H), 1.74–1.83(m, -CH₂, 4H), 3.97 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.48 (m, Hz, Ar–H, 2H), 6.52 (s, Ar–H, 2H), 7.21 (d, *J* = 8.1 Hz, Ar–H, 2H), 8.56 (s, -CHN, 2H), 11.46 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.67, 25.96, 29.04, 29.30, 29.54, 31.88, 68.37, 101.67, 108.20, 110.60, 133.60, 161.92, 162,38, 163.87. MS (LRFAB): M⁺ (m/z) = 552.57. Anal. Calcd. for C₃₄H₅₂N₂O₄: C, 73.87; H, 9.48; N, 5.07. Found: C, 73.51; H, 9.49; N, 4.99.

4.4.4 6, 6'-(1E,1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-dodecyloxy phenol) 1a (n = 12)

Pale yellow solids, yield 57%. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, -CH₃, 6H), 1.25–1.43 (m, -CH₂, 36H), 1.74–1.79 (m, -CH₂, 4H), 3.96 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.47 (d, J = 2.4 Hz, Ar–H, 2H), 6.50 (s, Ar–H, 2H), 7.18 (d, J = 9 Hz, Ar–H, 2H), 8.54 (s, –CHN, 2H), 11.46 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.68, 25.96, 29.05, 29.34, 29.58, 29.63, 31.91, 68.29, 101.62, 108.00, 110.79, 133.46, 161.77, 162.58, 163.57. MS (LRFAB): M⁺ (m/z) = 608.60. Anal. Calcd. for C₃₈H₆₀N₂O₄: C, 74.96; H, 9.93; N, 4.60. Found: C, 75.07; H, 10.12; N, 4.28.

4.4.5 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-tetra decyloxyphenol) 1a (n = 14)

Pale yellow solids, yield 61%. ¹H NMR (300 MHz, CDCl₃): δ 0.86 (t, *J* = 6.9 Hz, -CH₃, 6H), 1.24–1.43 (m, -CH₂, 44H), 1.73–1.82 (m, -CH₂, 4H), 3.97 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.48 (d, *J* = 3.6 Hz, Ar–H, 2H), 6.50 (s, Ar–H, 2H), 7.18 (d, *J* = 9.3 Hz, Ar–H, 2H), 8.55 (s, -CHN, 2H), 11.71 (bs, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.12, 22.69, 25.97, 29.05, 29.35, 29.58, 29.66, 31.92, 68.38, 101.67, 108.23, 110.59, 133.61 161.94, 162.35, 163.91. MS (LRFAB): M⁺ (m/z) = 664.68. Anal. Calcd. for C₄₂H₆₈N₂O₄: C, 75.86; H, 10.31; N, 4.21. Found: C, 74.37; H, 10.31; N, 3.96.

4.4.6. 6, 6'-(1E, 1'E)-hydrazine-1, 2-diylidenebis(methan-1-yl-1-ylidene)bis(3-hexa decyloxyphenol) 1a (n = 16)

Pale yellow solids, yield 62%. ¹**H** NMR (300 MHz, CDCl₃): δ 0.86 (t, *J* = 6.6 Hz, -CH₃, 6H), 1.24–1.43 (m, -CH₂, 52H), 1.73-1.79 (m, -CH₂, 4H), 3.97 (t, *J* = 6.6 Hz, -OCH₂, 4H), 6.48 (m, Hz, Ar-H, 2H), 6.51 (s, Ar-H, 2H), 7.20 (d, *J* = 8.4 Hz, Ar-H, 2H), 8.55 (s, -CHN, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.68, 25.96, 29.04, 29.35, 29.55, 29.67, 31.92, 68.34, 101.67, 108.08, 110.76, 133.54, 161.84, 162.58, 163.67. MS (LRFAB): M⁺ (m/z) = 720.87. Anal. Calcd. for C₄₆H₇₆N₂O₄: C, 76.62; H, 10.62; N, 3.88. Found: C, 76.52; H, 10.65; N, 3.89. **4.5. 6, 6'-(1E, 1'E)-1, 1'-(hydrazine-1, 2-diylidene)bis(ethan-1-yl-1-ylidene)bis(3-propoxy phenol) 1b (n = 3)**

Pale yellow solids, yield 64%. ¹H NMR (300 MHz, DMSO–d₆): δ 1.03 (t, *J*= 7.5 Hz, –CH₃, 6H), 1.75–1.87 (m, –CH₂, 4H), 2.50 (s, –CH₃, 6H), 3.94 (t, *J* = 6.6 Hz, –OCH₂, 4H), 6.45–6.49 (m, Ar–H, 4H), 7.50 (d, *J* = 9.3 Hz, Ar–H, 2H), 13.81 (s, Ar–OH, 2H). ¹³C NMR

(75 MHz, DMSO–d₆): δ 10.46, 14.62, 22.42, 69.60, 101.96, 107.14, 112.52, 130.05, 162.75, 162.83, 166.80.

4.5.1. 6,6'-(1E,1'E)-1,1'-(hydrazine-1,2-diylidene)bis(ethan-1-yl-1-ylidene)bis(3-

(dodecyloxy)phenol) 1b (n = 12)

Pale yellow solids, yield 63%. ¹H NMR (300 MHz, DMSO–d₆): δ 0.86 (t, *J* = 6.9 Hz, –CH₃, 6H), 1.25 (m, –CH₂, 36H), 1.41–1.43 (m, –CH₂, 4H), 2.66 (s, –CH₃, 6H), 4.01 (t, *J* = 8.4 Hz, –OCH₂, 4H), 6.55 (d, *J* = 8.7 Hz, Ar–H, 2H), 6.84 (s, Ar–H, 2H), 7.56 (d, *J* = 9.9 Hz, Ar–H, 2H). ¹³C NMR (75 MHz, DMSO–d₆): δ 14.11, 14.62, 22.68, 25.97, 29.07, 29.34, 29.62, 31.90, 68.15, 101.93, 107.16, 112.50, 130.05, 162.74, 162.84, 166.79.

4.6. 6, 6'-(1E, 1'E)-(1, 4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis (3-propoxyphenol) 2 (n = 3)

A solution of 2-hydroxy-4-propoxybenzaldehyde (0.2 g, 1.0 mmol) and benzene-1,4-diamine (0.06 g, 0.5 mmol) dissolved in 15 mL of absolute ethanol was stirred for 12 h. After cooling to room temperature, the crude solids were filtered. The products isolated as orange–yellow solids were obtained after crystallization from ethanol/acetone. Yield: 75%. ¹H NMR (300 MHz, CDCl₃): δ 1.03 (t, *J* = 7.2 Hz, –CH₃, 6H), 1.78–1.85 (m, –CH₂, 4H), 3.96 (t, *J* = 6.6 Hz, –OCH₂, 4H), 6.46–6.49 (m, Ar–H, 4H), 7.15–7.29 (m, Ar–H, 6H), 8.54 (s, –CHN, 2H), 13.70 (s, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃)): δ 10.45, 22.42, 69.71, 101.59, 107.68, 113.01, 121.97, 133.50, 146.62, 160.94, 163.67, 163.91. MS (LRFAB): M⁺ (m/z) = 431.40. Anal. Calcd. for C₂₆H₂₈N₂O₄: C, 72.20; H, 6.53; N, 6.48. Found: C, 72.36; H, 6.72; N, 6.24. **4.6.1 6, 6'-(1E, 1'E)-(1, 4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)**

bis(3-(octyloxy)phenol) 2 (n = 8)

Orange–yellow solids, yield 76%. ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, *J* = 6.3 Hz, –CH₃, 6H), 1.27–1.44 (m, –CH₂, 20H), 1.74–1.83 (m, –CH₂, 4H), 3.98 (t, *J* = 6.9 Hz, –OCH₂, 4H), 6.46–6.49 (m, Ar–H, 4H), 7.21–7.29 (m, Ar–H, 6H), 8.54 (s, –CHN, 2H), 13.70 (s, Ar–OH, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.67, 26.00, 29.08, 29.23, 29.34, 29.71, 31.82, 68.33, 101.58, 101.97, 107.82, 112.88, 121.98, 133.59, 146.44, 160.91, 163.85, 163.99. MS

(LRFAB): M⁺ (m/z) = 571.56. Anal. Calcd. for C₃₆H₄₈N₂O₄: C, 75.49; H, 8.45; N, 4.89. Found: C, 75.66; H, 8.75; N, 4.50.

4.6.2. 6, 6'-(1E, 1'E)-(1,4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) bis(3-tetradodecvloxyphenol) 2 (n = 14)

Orange–yellow solids, yield 78%. ¹H NMR (300 MHz, CDCl₃): δ 0.86 (t, *J* = 7.2 Hz, –CH₃, 6H), 1.24–1.44 (m, –CH₂, 44H), 1.75–1.78 (m, –CH₂, 4H), 3.99 (t, *J* = 6.6 Hz, –OCH₂, 4H), 6.46–6.51 (m, Ar–H, 4H), 7.21–7.30 (m, Ar–H, 6H), 8.53 (s, –CHN, 2H), 13.64 (s, Ar–OH, 2H). MS (LRFAB): M⁺ (m/z) = 739.80. Anal. Calcd. for C₄₈H₇₂N₂O₄: C, 77.79; H, 9.79; N, 3.78. Found: C, 77.86; H, 9.86; N, 3.68.

4.7. 4, 4'-Bis((E)-2-hydroxy-4-propoxybenzylideneamino)biphenyl-3, 3'-diol 3 (n = 3)

A mixture of 2-hydroxy-4-propoxybenzaldehyde (0.2 g, 1.11 mmol), 4,4'-diaminobiphenyl-3,3'-diol (0.12 g, 0.55 mmol) and catalytic amount of I₂ dissolved in 10 mL of DMSO was stirred under nitrogen for 24 h. The solution was poured into ice water then the crude solids was filtered, washed with methanol. The products isolated as orange solids was obtained after recrystallization from THF. Yield: 77%, ¹H NMR (300 MHz, DMSO–d₆): δ 0.98 (t, *J* = 7.5 Hz, –CH₃, 6H), 1.70-1.77 (m, –CH₂, 4H), 3.97 (t, *J* = 6.3 Hz, –OCH₂, 4H), 6.38 (s, Ar–H, 2H), 6.47(d, *J* = 4.35 Hz, Ar–H, 2H), 7.12 (m, Ar–H, 4H), 7.45 (d, *J* = 2.85 Hz, Ar–H, 4H), 8.90 (s, –CHN, 2H), 9.92 (bs, Ar–OH, 2H). MS (LRFAB): M⁺ (m/z) = 523.69. Anal. Calcd. for C₃₂H₃₂N₂O₆: C, 71.09; H, 5.97; N, 5.18. Found: C, 69.32; H, 6.01; N, 4.89.

4.7.1. 4, 4'-Bis(**(E)-2-hydroxy-4-(octyloxy)benzylideneamino)biphenyl-3, 3'-diol 3 (n = 8)** Orange solids, yield 76%. ¹H NMR (300 MHz, DMSO–d₆): δ 0.85 (t, *J* = 6.9 Hz, –CH₃, 6H), 1.23–1.45 (m, –CH₂, 20H), 1.71 (m, –CH₂, 4H), 4.00 (t, *J* = 5.4 Hz, –OCH₂, 4H), 6.37–7.62 (m, Ar–H, 12H), 8.90 (s, –CHN, 2H), 9.98 (bs, Ar–OH, 2H). Anal. Calcd. for C₄₂H₅₂N₂O₆: C, 74.09; H, 7.70; N, 4.11. Found: C, 73.28; H, 7.66; N, 3.98.

4.7.2. 4, 4'-Bis((E)-2-hydroxy-4-(tetradecyloxy)benzylideneamino)biphenyl-3, 3'-diol 3 (n = 14)

Orange solids, yield 75%. ¹H NMR (300 MHz, DMSO-d₆): δ 0.85 (t, *J* = 6.9 Hz, -CH₃, 6H),

1.24 (m, –CH₂, 44H), 1.68–1.72 (m, –CH₂, 4H), 4.02 (t, J = 5.7 Hz, –OCH₂, 4H), 6.37–7.62 (m, Ar–H, 12H), 8.87 (s, –CHN, 2H), 9.99 (bs, Ar–OH, 2H), 14.51 (bs, Ar–OH, 2H). Anal. Calcd. for C₅₄H₇₆N₂O₆: C, 76.38; H, 9.02; N, 3.30. Found: C, 75.73; H, 9.08; N, 3.22 **4.8.3**, **3'-bis((E)-2-hydroxy-4-propoxybenzylideneamino)biphenyl-4**, **4'-diol 4 (n = 3)** A mixture of 2-hydroxy-4-propoxybenzaldehyde (0.2 g, 1.11 mmol), 3,3'-diaminobiphenyl-4,4'-diol (0.12 g, 0.55 mmol) and catalytic amount of I₂ dissolved in 10 mL of DMSO was stirred under nitrogen for 24 h. The solution was poured into ice water then the crude product was filtered, washed with acetone to afford yellow solid. Yield 33%. ¹H NMR (300 MHz, DMSO–d₆): δ 0.98 (t, J = 7.2 Hz, –CH₃, 6H), 1.68–1.78 (m, –CH₂, 4H), 3.98 (t, J = 6.6 Hz, –OCH₂, 4H), 6.39 (s, Ar–H, 2H), 7.46 (d, J = 4.35 Hz, Ar–H, 4H),7.00 (d, J = 4.2 Hz, Ar–H, 2H), 7.41 (d, J = 4.1 Hz, Ar–H, 2H), 7.46 (d, J = 4.35 Hz, Ar–H, 2H), 7.65 (s, Ar–H, 2H), 8.97 (s, –CHN, 2H), 9.78 (s, Ar–OH, 2H), 14.40 (s, Ar–OH, 2H). ¹³C NMR (75 MHz, DMSO-d₆): δ 10.40, 21.98, 69.23, 101.59, 106.95, 113.02, 116.70, 125.15, 131.74, 134.03, 134.24, 149.60, 160.23, 163.41, 165.94 MS (LRFAB): M⁺ (m/z) = 522.78. Anal. Calcd. for C₃₂H₃₂N₂O₆: C, 71.09; H, 5.97; N, 5.18. Found: C, 69.32; H, 6.01; N, 4.89.

4.8.1. 3, 3'-Bis((E)-2-hydroxy-4-octyloxybenzylideneamino)biphenyl-4, 4'-diol 4 (n = 8) Yellow solids, yield: 38%. ¹H NMR (300 MHz, DMSO–d₆): δ 0.86 (t, *J* = 6.9 Hz, –CH₃, 6H), 1.26–1.40 (m, –CH₂, 20H), 1.66–1.75(m, –CH₂, 4H), 4.00 (t, *J* = 6.6 Hz, –OCH₂, 4H), 6.38 (s, Ar–H, 2H), 6.46 (d, *J* = 8.4 Hz, Ar–H, 2H), 7.00 (d, *J* = 8.4 Hz, Ar–H, 2H), 7.41 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.45 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.66 (s, Ar–H, 2H), 8.97(s, –CHN, 2H), 9.85 (s, Ar–OH, 2H), 14.44 (s, Ar–OH, 2H). ¹³C NMR (75 MHz, DMSO–d₆): δ 13.98, 22.11, 25.50, 28.56, 28.68, 31.26, 67.72, 101.52, 106.92, 112.98, 116.66, 125.09, 131.67, 133.95, 134.25, 149.57, 160.25, 163.33, 165.76. Anal. Calcd. for C₄₂H₅₂N₂O₆: C, 74.09; H, 7.70; N, 4.11. Found: C, 73.97; H, 7.73; N, 4.08.

4.8.2. 3, 3'-Bis((E)-2-hydroxy-4-tetradecyloxybenzylideneamino)biphenyl-4, 4'-diol 4 (n = 14)

Yellow solids, yield: 36%. ¹H NMR (300 MHz, DMSO-d₆): δ 0.85 (t, *J* = 6.6 Hz, -CH₃, 6H),

1.23–1.38 (m, –CH₂, 44H), 1.68–1.72 (m, –CH₂, 4H), 4.00 (t, J = 6.3 Hz, –OCH₂, 4H), 6.37 (s, Ar–H, 2H), 6.44 (d, J = 6.3 Hz, Ar–H, 2H), 6.95 (d, J = 8.4 Hz, Ar–H, 2H), 7.44–7.48(m, Ar–H, 4H), 7.62 (s, Ar–H, 2H), 8.94 (s, –CHN, 2H), 9.99 (s, Ar–OH, 2H), 14.42 (s, Ar–OH, 2H). Anal. Calcd. for C₅₄H₇₆N₂O₆: C, 76.38; H, 9.02; N, 3.30. Found: C, 75.90; H, 8.98; N, 3.24.

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