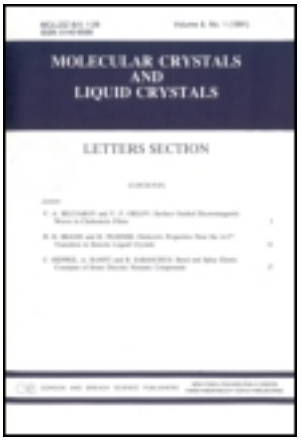

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Synthesis, Characterization, and Mesomorphic Investigations of Calamitic Liquid Crystals - methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino) benzoates and Their Copper(II) and Nickel(II) Complexes

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Synthesis, Characterization, and Mesomorphic Investigations of Calamitic Liquid Crystals – methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino) benzoates and Their Copper(II) and Nickel(II) Complexes

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A new series of Schiff's base mesogenic ligands with a polar methyl ester as an end group, methyl 4-(4′-(alkoxy)-2 hydroxybenzylideneamino) benzoates, C_nLH (n = 6, 8, 10, 12, 14, 16) and their copper(II) and nickel(II) complexes have been synthesized. They were characterized by elemental analyses, Fourier transform infrared (FT-IR), ^1H and ^{13}C nuclear magnetic resonance, and UV-VIS spectroscopy. The mesomorphic properties of these compounds were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The ligands exhibit an enantiotropic SmA mesophase with a high-temperature range and thermal stability. The square planar copper(II) complexes show enantiotropic SmA mesophase, but the nickel(II) complexes are nonmesogenic in nature. The thermal stability of the compounds was also determined by thermo gravimetric analyses. Density functional theory (DFT) calculations were performed using GAUSSIAN-03 program at B3LYP level to obtain the stable electronic structure of the ligand and their metal complexes.

Keywords Density functional theory; differential scanning calorimetry; enantiotropic mesophase; metallomesogen; polarizing optical microscopy

1. Introduction

Liquid crystals containing transition metals, called as metallomesogens, have gained attention because of their unusual geometries and novel properties such as color, paramagnetism, fluidity, large birefringence, and polarizability. In addition to functional properties such as spin cross-over, ferroelectricity, photorefractivity, nonlinear optical characteristics, large magnetic anisotropy, and luminescent mesophases. Since the metallomesogens are achieved through changes of molecular conformation, shape, and structure, their physico-chemical properties can be tuned by the choice of metal ions, substituents, and position of substituents on core moieties [1–3]. Schiff base ligands provide a wide range of ways to modify liquid crystalline properties [4, 5]. The organic liquid crystalline species whose rigid core is

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salicylaldimine [6] has been found convenient starting material for the preparation of metallomesogens. Copper (II), nickel (II), vanadyl (IV), palladium (II) [7–12], and iron (III) [13] complexes of salicylideneamine derivatives have been reported to show liquid crystalline properties. In 1984, Ovchinnikov and coworkers were first to exploit the coordination possibilities of salicylideneanilines and they reported the first imino-derived metallomesogens [14]. As was first observed by Ovchinnikov, N-(alkoxyphenyl)-4-alkoxysalicylaldimines mainly show smectic mesomorphism when coordinated to copper(II) [15–18]. When both chains in the ligands are short the compounds are not liquid crystalline. If one of the tails is elongated, a smectic A phase is observed. In addition, a smectic C phase is observed for cases where both alkoxy tails are long. The molecular shape of these complexes is considered to be two roughly parallel rodlike moieties mutually head to tail oriented and connected by the metals. They are classified as lateral–lateral fused mesogens, the wider class of nondiscotic metallomesogens [19]. In such molecules, the metallic core actually acts as a spacer between the two elongated frameworks. In this paper, we describe the synthesis and mesomorphic properties of a series of new salicylaldimines and their copper(II) and nickel(II) complexes. We have replaced one chain by $-CO_2CH_3$ group. It would be interesting as the polar nature of the carbonyl group plays a vital role in ferroelectric liquid crystals and this polarity can affect the mesomorphic and physicochemical properties of metal complexes in an unpredictable manner. Their thermotropic LC properties were examined by using various experimental techniques with the aim of understanding the structure-property relationship and developing novel materials based on this class of compounds.

2. Experimental Details

2.1. Materials

All reagents were purchased from commercial sources and were used as received: 2,4-dihydroxybenzaldehyde, methyl 4-aminobenzoate,1-bromoalkanes, and all metal acetates are from Aldrich Chemicals, USA. All other solvents and reagents were purchased from Merck. The solvents were dried using standard methods when required [20].

2.2. Techniques

Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyzer. IR spectra (4000–400 cm^{-1}) were recorded on a Varian 3100 FT-IR Excalibur series spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a JEOL FT-NMR AL 300 MHz spectrometer using tetramethylsilane as the internal standard. Electronic spectra were recorded on an (UV)-1700 Pharma Spec. Shimadzu UV-VIS spectrophotometer. Room temperature magnetic susceptibility measurements were performed on a Cahn Faraday balance using $Co[Hg(SCN)_4]$ as standard. The magnetic susceptibility was corrected for diamagnetism using Pascal's constants. Differential scanning calorimetry (DSC) thermograms were recorded with a Mettler Toledo TC 15 TA differential scanning calorimeter at the rate of 5.0 K min^{-1} under nitrogen atmosphere using spec pure grade indium as standard and the samples were taken in close-lid aluminum pans. The transition temperatures from DSC thermograms have been determined with an accuracy of ± 0.1 K. The mesophase type was identified by visual comparison with known phase standards using an HT 30.01 NTT 268 Lomo polarizing optical microscope (POM) fitted with a hot stage having temperature

controlling accuracy of 0.1 K. Thermogravimetric analysis (TGA) was performed using a PerkinElmer-STA 6000 apparatus under high-purity nitrogen. The samples were heated from room temperature to 800°C at 10°C/min and the weight data were collected continuously. The onset of decomposition was defined as the decomposition temperature (*Td*). Quantum chemical calculations were carried out using density functional theory (DFT) as implemented in GAUSSIAN-03 package.

2.3. Synthesis

2.3.1. Synthesis of 4-(decyloxy)-2-hydroxybenzaldehyde. Potassium bicarbonate (55 mmol, 5.51 g) was added to a solution of equimolar amounts of 2,4-dihydroxy benzaldehyde (50 mmol, 6.91 g) and 1-bromodecane (50 mmol, 10.4 mL) in dry 2-butanone(100 mL). The mixture was refluxed for 30 h in the presence of KI (0.1–0.2 g) as a catalyst and filtered while hot to remove the insoluble solids. Dilute hydrochloric acid (6 N) was added to the filtrate until the point of neutralization and the product was then extracted twice with $CHCl_3$ (100 mL portions). The chloroform extract was concentrated to obtain a yellow oil, which was purified by column chromatography over SiO_2 eluting first with n-hexane and then with a mixture of n-hexane and chloroform (v/v, 1/1); evaporation of this purified extract finally yielded 4-(decyloxy)-2-hydroxybenzaldehyde as a pale yellow oil; yield: 62% (8.63 g).

All other members of the homologous series 4-hexyloxy-2-hydroxybenzaldehyde, 4-octyloxy-2-hydroxybenzaldehyde, 4-dodecyloxy-2-hydroxybenzaldehyde, 4-tetradecy loxy-2-hydroxybenzaldehyde, and 4-hexadecyloxy-2-hydroxybenzaldehyde were prepared using the above procedure.

IR (KBr, cm^{-1}): 3450 (–OH), 2939, 2858 (aliphatic C–H), 1690 (C=O), 1606, 1560 (Ph), 1317, 1248 (–OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 11.24 (s, 1H), 9.88 (s, 1H), 7.62 (d, 1H) 6.98 (d, 1H), 6.92 (s, 1H), 4.07 (t, 2H), 1.85–1.26 (m, 16H), 0.90 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 195.47, 163.92, 163.19, 134.91, 132.46, 118.59, 110.88, 68.41, 31.90, 29.60, 25.96, 22.68, 14.10.

2.3.2. Synthesis of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate, C_{10}LH (1c). 4-(decyloxy)-2-hydroxybenzaldehyde (2.78 g, 10 mmol) and methyl 4-amino benzoate (1.51 g, 10 mmol) were mixed together in ethanol (10 mL). To this, 6–8 drops of glacial acetic acid were added as a catalyst. The reaction mixture was refluxed for 4 h. The color of solution becomes yellow. The yellow precipitate that formed on cooling was filtered off, washed with cold ethanol, and recrystallized from ethanol-chloroform mixture (1/1, v/v).

IR (KBr, cm^{-1}): 3416 (–OH), 2955, 2927, 2856 (aliphatic C–H), 1723 (ester, C=O), 1628 (C=N), 1600, 1569 (Ph), 1284, 1236 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 13.41(s, 1H, –OH), 8.53 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $-C_6H_4$), 7.28 (m, 3H, $-C_6H_3$), 6.50 (d, J_1 (H, H) = 8.2 Hz, 2H, $-C_6H_3$), 4.02–3.98 (t, 2H, $-OCH_2$), 3.93 (s, 3H, $COOCH_3$), 1.85 (m, 8H, $-OCH_2C\underline{H}_2$), 1.55–1.27 (m, 8H), 0.89 (t, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.65, 164.04, 162.79, 152.58, 133.87, 131.01, 127.73, 120.96, 112.75, 108.00, 101.51, 77.42, 76.57, 68.33, 52.12, 31.88, 29.53, 25.96, 22.66. 14.10; Elemental analyses: calculated for $C_{25}H_{33}NO_4$ (%) – C, 73.02; H, 8.09; N, 3.40; Found C, 72.91; H, 8.20; N, 3.48.

2.3.3. Synthesis of methyl 4-(4′-(hexyloxy)-2-hydroxybenzylideneamino)benzoate, C_6LH (1a). IR (KBr, cm^{-1}): 3417 (OH), 2955, 2927, 2857 (aliphatic C–H), 1723 (ester, C=O), 1628 (C=N), 1600, 1573 (Ph), 1284, 1243 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H

13.41 (s, 1H, –OH), 8.53 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $–C_6H_4$), 7.29 (m, 3H, $–C_6H_3$), 6.50 (d, J_1 (H, H) = 8.2 Hz, 2H, $–C_6H_3$), 4.02–4.00 (t, 2H, $–OCH_2$), 3.92 (s, 3H, $COOCH_3$) 1.82–1.34 (m, 8H, $–[CH_2]_4$), 0.91 (t, 3H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.63, 164.16, 162.79, 152.62, 133.92, 131.06, 127.73, 120.96, 112.74, 107.98, 101.52, 77.43, 76.59, 68.32, 52.11, 31.91, 29.74, 25.73, 22.81, 14.17; Elemental analyses: calculated for $C_{21}H_{25}NO_4$(%) – C, 71.01; H, 7.09; N, 3.94; Found C, 71.21; H, 7.25; N, 3.86.

2.3.4. Synthesis of Methyl 4-(4′-(octyloxy)-2-hydroxybenzylideneamino)benzoate, C_8LH (1b). IR (KBr, cm^{-1}): 3419 (–OH), 2955, 2926, 2857 (aliphatic C–H), 1723 (ester, C=O), 1629(C=N), 1601, 1572 (Ph), 1283, 1236 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 13.42 (s, 1H, –OH), 8.52 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $–C_6H_4$), 7.29 (m, 3H, $–C_6H_3$), 6.50 (d, J_1 (H, H) = 8.2 Hz, 2H, $–C_6H_3$), 4.02–4.00 (t, 2H, $–OCH_2$), 3.92 (s, 3H, $COOCH_3$) 1.82–1.34 (m, 12H, $–[CH_2]_6$), 0.91 (t, 3H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.64, 164.15, 162.79, 152.62, 133.93, 131.06, 127.73, 120.97, 112.74, 107.98, 101.52, 77.43, 76.59, 68.32, 52.11, 31.91, 29.74, 29.42, 26.01, 22.81, 14.17; Elemental analyses: calculated for $C_{23}H_{29}NO_4$(%) – C, 72.08; H, 7.63; N, 3.66; Found C, 72.23; H, 7.71; N, 3.75.

2.3.5. Synthesis of Methyl 4-(4′-(dodecyloxy)-2-hydroxybenzylideneamino)benzoate, $C_{12}LH$ (1d). IR (KBr, cm^{-1}): 3420 (–OH), 2955, 2919, 2849 (aliphatic C–H), 1723 (ester, C=O), 1628 (C=N), 1601, 1573 (Ph), 1284, 1236 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 13.41 (s, 1H, –OH), 8.52 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $–C_6H_4$), 7.29 (m, 3H, $–C_6H_3$), 6.50 (d, J_1 (H, H) = 8.2 Hz, 2H, $–C_6H_3$), 4.02–4.00 (t, 2H, $–OCH_2$), 3.92 (s, 3H, $COOCH_3$) 1.82–1.34 (m, 20H, $–[CH_2]_{10}$), 0.91 (t, 3H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.63, 164.168 162.73, 152.62, 133.91, 131.06, 127.73, 120.96, 112.74, 107.97, 101.52, 77.43, 76.59, 68.32, 52.11, 31.91, 29.74, 29.42, 26.01, 22.81, 14.17; Elemental analyses: calculated for $C_{27}H_{37}NO_4$(%) – C, 73.83; H, 8.49; N, 3.19; Found C, 73.96; H, 8.20; N, 3.02.

2.3.6. Synthesis of Methyl 4-(4′-(tetradecyloxy)-2-hydroxybenzylideneamino)benzoate, $C_{14}LH$ (1e). IR (KBr, cm^{-1}): 3421 (–OH), 2955, 2918, 2849 (aliphatic C–H), 1724 (ester, C=O), 1628 (C=N), 1601, 1573 (Ph), 1284, 1236 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 13.41 (s, 1H, –OH), 8.52 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $–C_6H_4$), 7.29 (m, 3H, $–C_6H_3$), 6.50 (d, J_1 (H, H) = 8.2 Hz, 2H, $–C_6H_3$), 4.02–4.00 (t, 2H, $–OCH_2$), 3.92 (s, 3H, $COOCH_3$) 1.82–1.26 (m, 24H, $–[CH_2]_{12}$), 0.88 (t, 3H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.62, 164.19, 162.78, 152.62, 133.92, 131.08, 127.73, 120.96, 112.75, 107.98, 101.52, 77.43, 76.59, 68.32, 52.11, 31.91, 29.74, 29.42, 26.01, 22.81, 14.17; Elemental analyses: calculated for $C_{29}H_{41}NO_4$(%) – C, 74.54; H, 8.84; N, 2.99; Found C, 74.32; H, 8.60; N, 2.90.

2.3.7. Synthesis of Methyl 4-(4′-(hexadecyloxy)-2-hydroxybenzylideneamino)benzoate, $C_{16}LH$ (1f). IR (KBr, cm^{-1}): 3419 (–OH), 2955, 2918, 2849 (aliphatic C–H), 1724 (ester, C=O), 1628 (C=N), 1601, 1574 (Ph), 1284, 1236 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 13.41 (s, 1H, –OH), 8.53 (s, 1H, –CH=N), 8.09 (d, J_1 (H, H) = 8.4 Hz, 2H, $–C_6H_4$), 7.29 (m, 3H, $–C_6H_3$), 6.49 (d, J_1 (H, H) = 8.2 Hz, 2H, $–C_6H_3$), 4.02–3.98 (t, 2H, $–OCH_2$), 3.92 (s, 3H, $COOCH_3$) 1.82–1.26 (m, 28H, $–[CH_2]_{14}$), 0.86 (t, 3H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.61, 164.16, 162.79, 152.65, 133.92, 131.06, 127.74, 120.96, 112.73, 107.98, 101.52, 77.42, 76.59, 68.32, 52.11, 31.91, 29.74, 29.42, 26.01,

22.81, 14.17; Elemental analyses: calculated for $C_{31}H_{45}NO_4$(%) – C, 75.17; H, 9.16; N, 2.83; Found C, 75.65; H, 8.96; N, 3.01.

Procedure for preparation of nickel and copper complexes

To a solution (20 mL) of methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino)benzoate (2 eq) in hot methanol/chloroform (1/1,v/v) stirred at room temperature was added metal acetate (1 eq) in methanol (10 mL). The mixture was stirred at room temperature for 2 h. The resulting compound was filtered off, washed with methanol and recrystallized from chloroform/ethanol (1/1,v/v). All the copper(II) and nickel(II) complexes are synthesized by the above method.

2.3.8. Bis[methyl 4-(4′-(hexyloxy)-2-hydroxybenzylideneamino)benzoato]copper(II), (C_6 L)$_2$Cu (2a). Yield: 71% (brown colored solid). IR (KBr, cm^{-1}): 2924, 2854 (aliphatic C–H), 1720 (ester, C=O), 1609 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{21}H_{24}NO_4)_2Cu$ (%) – C, 65.31; H, 6.26; N, 3.63, Cu, 8.23; Found C, 65.58; H, 6.46; N, 3.76, Cu, 8.42.

2.3.9. Bis[methyl 4-(4′-(octyloxy)-2-hydroxybenzylideneamino)benzoato]copper(II), (C_8 L)$_2$Cu (2b). Yield: 70% (brown colored solid). IR (KBr, cm^{-1}): 2924, 2854 (aliphatic C–H), 1720 (ester, C=O), 1611 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{23}H_{28}NO_4)_2Cu$ (%) – C, 66.69; H, 6.81; N, 3.38, Cu, 7.67; Found C, 66.46; H, 6.66; N, 3.56, Cu, 7.42.

2.3.10. Bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoato]copper(II), (C_{10}L)$_2$Cu (2c). Yield: 70% (brown colored solid). IR (KBr, cm^{-1}): 2924, 2854 (aliphatic C–H), 1720 (ester, C=O), 1610 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{25}H_{32}NO_4)_2Cu$ (%) – C, 67.89; H, 7.29; N, 3.17, Cu, 7.18; Found C, 67.96; H, 6.99; N, 3.36, Cu, 7.35.

2.3.11. Bis[methyl 4-(4′-(dodecyloxy)-2-hydroxybenzylideneamino)benzoato]copper(II), (C_{12}L)$_2$Cu (2d). Yield: 72% (brown colored solid). IR (KBr, cm^{-1}): 2922, 2849 (aliphatic C–H), 1712 (ester, C=O), 1609 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{27}H_{36}NO_4)_2Cu$ (%) – C, 68.95; H, 7.72; N, 2.98, Cu, 6.76; Found C, 69.16; H, 7.58; N, 3.16, Cu, 7.05.

2.3.12. Bis[methyl 4-(4′-(tetradecyloxy)-2-hydroxybenzylideneamino)benzoato]copper (II), (C_{14}L)$_2$Cu (2e). Yield: 69% (brown colored solid). IR (KBr, cm^{-1}): 2918, 2850 (aliphatic C–H), 1719 (ester, C=O), 1611 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{29}H_{40}NO_4)_2Cu$ (%) – C, 69.89; H, 8.09; N, 2.81, Cu, 6.38; Found C, 69.56; H, 7.98; N, 3.06, Cu, 6.79.

2.3.13. Bis[methyl 4-(4′-(hexadecyloxy)-2-hydroxybenzylideneamino)benzoato]copper (II), (C_{16}L)$_2$Cu (2f). Yield: 70% (brown colored solid). IR (KBr, cm^{-1}): 2920, 2850 (aliphatic C–H), 1719 (ester, C=O), 1611 (C=N), 1594, 1534 (Ph), 1290, 1242 (OPh). Elemental analyses: calculated for $(C_{31}H_{44}NO_4)_2Cu$ (%) - C, 70.72; H, 8.42; N, 2.66, Cu, 6.03; Found C, 70.43; H, 8.08; N, 3.01, Cu, 6.42.

2.3.14. Bis[methyl 4-(4′-(hexyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3a). Yield: 68% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1723 (ester, C=O),

1612 (C=N), 1574, 1512 (Ph), 1290, 1244 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.89 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.08 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.35 (s, 2H, $–C_6H_3$), 6.30 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.98–3.91 (t, 4H, $–OCH_2$), 3.85 (s, 6H, $COOCH_3$), 1.78–1.26 (m, 32H, $–[CH_2]_{16}$), 0.88 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.67, 167.12, 166.44, 152.82, 133.31, 131.31 127.76, 121.10, 113.02, 107.90, 104.80, 77.42, 76.58, 68.20, 52.16, 31.96, 29.67, 25.95, 22.68, 14.15. Elemental analyses: calculated for $(C_{21}H_{24}NO_4)_2Ni$ (%) – C, 65.72; H, 6.30; N, 3.65; Ni, 7.65; Found C, 65.46; H, 6.43; N, 3.39; Ni, 7.33.

2.3.15. Bis[methyl 4-(4′-(octyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3b). Yield: 65% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1721 (ester, C=O), 1613 (C=N), 1574, 1512 (Ph), 1290, 1245 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.89 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.07 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.35 (s, 2H, $–C_6H_3$), 6.30 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.98–3.91 (t, 4H, $–OCH_2$), 3.84 (s, 6H, $COOCH_3$), 1.78–1.26 (m, 32H, $–[CH_2]_{16}$), 0.88 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.65, 167.14, 166.43, 152.80, 133.31, 131.33 127.76, 121.10, 113.04, 107.91, 104.81, 77.45, 76.58, 68.20, 52.16, 31.96, 29.68, 25.95, 22.68, 14.15. Elemental analyses: calculated for $(C_{23}H_{28}NO_4)_2Ni$ (%) – C, 67.08; H, 6.85; N, 3.40; Ni, 7.13; Found C, 66.86; H, 6.51; N, 3.13; Ni, 7.33.

2.3.16. Bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3c). Yield: 66% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1720 (ester, C=O), 1611 (C=N), 1574, 1514 (Ph), 1292, 1244 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.89 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.08 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.36 (s, 2H, $–C_6H_3$), 6.30 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.98–3.92 (t, 4H, $–OCH_2$), 3.85 (s, 6H, $COOCH_3$), 1.78–1.27 (m, 32H, $–[CH_2]_{16}$), 0.87 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.67, 167.16, 166.46, 152.82, 133.31, 131.31 127.76, 121.10, 113.02, 107.90, 104.81, 77.42, 76.59, 68.20, 52.16, 31.96, 29.67, 25.95, 22.68, 14.15. Elemental analyses: calculated for $(C_{25}H_{32}NO_4)_2Ni$ (%) – C, 68.26; H, 7.33; N, 3.18; Ni, 6.67; Found C, 67.96; H, 6.99; N, 3.03; Ni, 6.33.

2.3.17. Bis[methyl 4-(4′-(dodecyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3d). Yield: 69% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1723 (ester, C=O), 1613 (C=N), 1573, 1512 (Ph), 1291, 1243 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.88 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.08 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.36 (s, 2H, $–C_6H_3$), 6.31 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.97–3.91 (t, 4H, $–OCH_2$), 3.85 (s, 6H, $COOCH_3$), 1.77–1.26 (m, 32H, $–[CH_2]_{16}$), 0.89 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.68, 167.13, 166.43, 152.83, 133.31, 131.32, 127.75, 121.10, 113.03, 107.90, 104.81, 77.43, 76.58, 68.20, 52.16, 31.96, 29.67, 25.95, 22.69, 14.13. Elemental analyses: calculated for $(C_{27}H_{36}NO_4)_2Ni$ (%) – C, 69.30; H, 7.76; N, 2.99; Ni, 6.27; Found C, 68.98; H, 7.41; N, 3.13; Ni, 6.37.

2.3.18. Bis[methyl4-(4′-(tetradecyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3e). Yield: 65% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1722 (ester, C=O), 1612 (C=N), 1574, 1514 (Ph), 1290, 1244 (OPh). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.89 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.08 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.35 (s, 2H, $–C_6H_3$), 6.30 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.98–3.91 (t, 4H, $–OCH_2$), 3.85 (s, 6H, $COOCH_3$), 1.78–1.26 (m, 32H, $–[CH_2]_{16}$), 0.88 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.67, 167.12, 166.44, 152.82, 133.31,

131.31 127.76, 121.10, 113.02, 107.90, 104.80, 77.42, 76.58, 68.20, 52.16, 31.96, 29.67, 25.95, 22.68, 14.15. Elemental analyses: calculated for $(C_{29}H_{40}NO_4)_2Ni$ (%) – C, 70.22; H, 8.13; N, 2.82; Ni, 5.91; Found C, 69.96; H, 7.97; N, 3.03; Ni, 6.21.

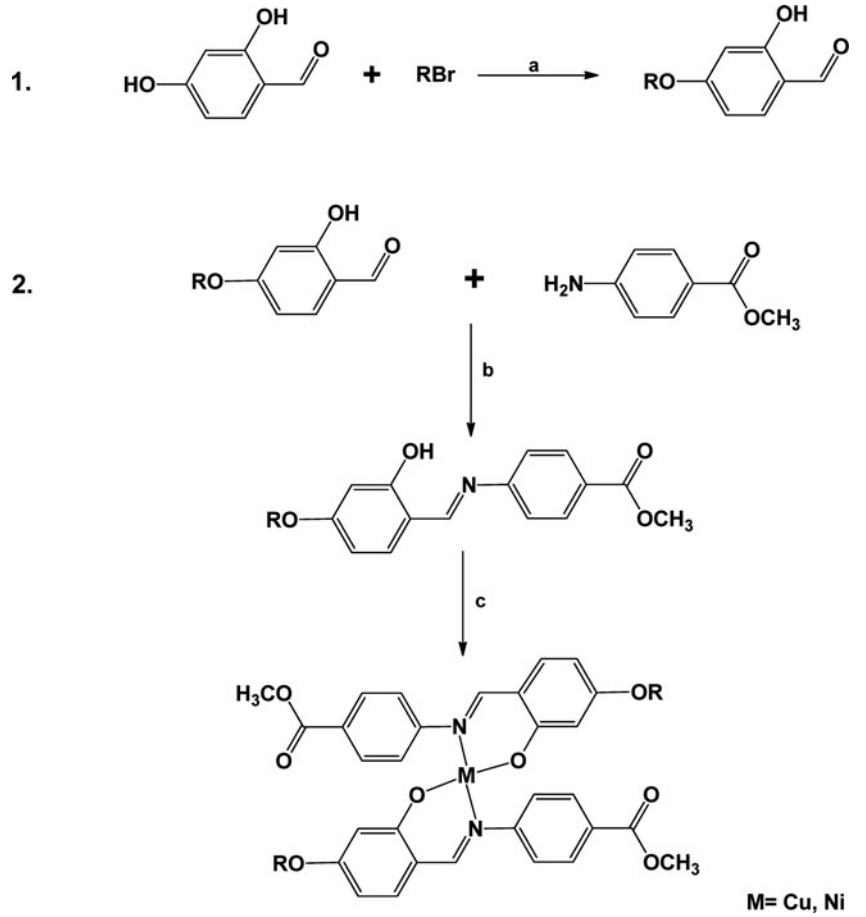
2.3.19. Bis[methyl4-(4′-(hexadecyloxy)-2-hydroxybenzylideneamino)benzoato]nickel(II) (3f). Yield: 68% (orange solid), IR (KBr, cm^{-1}): 2928, 2862 (aliphatic C–H), 1722 (ester, C=O), 1611 (C=N), 1575, 1512 (Ph), 1293, 1244 (OPh). ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ_H 8.24 (s, 2H, –CH=N), 7.89 (d, J_1 (H, H) = 8.4 Hz, 4H, $–C_6H_4$), 7.08 (d, J_1 (H, H) = 8.4 Hz, 6H, $–C_6H_4$), 6.34 (s, 2H, $–C_6H_3$), 6.31 (d, J_1 (H, H) = 9.0 Hz, 2H, $–C_6H_3$), 3.98–3.92 (t, 4H, $–OCH_2$), 3.85 (s, 6H, $COOCH_3$), 1.78–1.26 (m, 32H, $–[CH_2]_{16}$), 0.88 (t, 6H, $–CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 167.64, 167.17, 166.43, 152.82, 133.33, 131.31 127.76, 121.12, 113.02, 107.90, 104.80, 77.42, 76.58, 68.20, 52.16, 31.96, 29.67, 25.95, 22.68, 14.15. Elemental analyses: calculated for $(C_{31}H_{44}NO_4)_2Ni$ (%) – C, 71.05; H, 8.46; N, 2.67; Ni, 5.60; Found C, 69.86; H, 8.08; N, 2.98; Ni, 5.92.

3. Results and Discussion

3.1. Synthesis and Characterization

The synthetic route for preparation of Schiff base ligands methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate and their metal complexes is outlined in Scheme 1.

Alkylation of 2,4-dihydroxybenzaldehyde with decyl bromide in presence of strong base in dry 2-butanone allowed us to obtain a reasonable yield of 4-(decyloxy)-2-hydroxybenzaldehyde. The Schiff base was obtained by the condensation of methyl 4-aminobenzoate with 4-(decyloxy)-2-hydroxybenzaldehyde in refluxing ethanol. The metal complexes were prepared by reaction of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate with corresponding metal acetate in refluxing ethanol. The copper and nickel complexes were then isolated as brown and orange solid, respectively, by recrystallization from absolute ethanol in good yield (65%–72%). The ligands and their metal complexes were characterized by elemental analyses and standard spectroscopic techniques. The IR spectrum of 4-(decyloxy)-2-hydroxybenzaldehyde shows absorption bands at 3450, (2939, 2858), 1690, (1606, 1560), (1317, 1248) cm^{-1} assigned to ν (OH), ν (aliphatic C–H stretch), ν (C=O aldehyde), ν (Ph), and ν (OPh), respectively. The IR spectrum of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate shows absorption bands at 3416, (2955, 2856), 1723, 1628, (1600,1569), (1284,1236) cm^{-1} assigned to ν (OH), ν (aliphatic C–H stretch), ν (C=O) of phenyl ester, ν (C=N), ν (Ph), and ν (OPh) modes, respectively. The disappearance of the band at 1690 cm^{-1} due to ν (CH=O) and appearance of a new band at 1628 cm^{-1} due to ν (C=N) indicate condensation of aldehyde with amine forming Schiff base. The proton NMR of 4-(decyloxy)-2-hydroxybenzaldehyde exhibit peaks δ 11.24 (s), 9.88(s), 7.61–6.92 (m), 4.07(t), 1.85–1.26 (m), and 0.90(t) ppm which are assigned to –OH, –CHO, ring, $–OCH_2$, $–[CH_2]_n$, and $–CH_3$ protons, respectively. The proton NMR spectrum of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate exhibits peaks at δ 13.41(s), 8.53(s), 8.09–6.50(m), 4.02(t), 3.93(s), 1.84–1.27(m), 0.88(t) ppm which are assigned to –OH, –CH=N, ring, $–OCH_2$, $–COOCH_3$, $–[CH_2]_n$, and $–CH_3$ protons, respectively. The signals due to Schiff base formation is observed at 8.64 ppm which corresponds to *o*-hydroxy benzylidene. The length of alkyl chain has no significant effect on the position of the signals due to –OH, –CH=N, ring, $–OCH_2$, $–[CH_2]_n$, and $–CH_3$ protons. The IR spectrum of copper (II) complexes shows absorption bands at (2924, 2854), 1720, 1609, (1594, 1534), and (1290, 1242) cm^{-1} which are assigned to ν (aliphatic



Scheme 1. *Reactions and reagents:* (a) potassium bicarbonate(1.1 equiv.), refluxing in acetone, 24 h, 60%–67%; (b) acetic acid (3 drops), refluxing in EtOH, 4 h, 92%; (c) $Cu(OAc)_2.H_2O$ or $Ni(OAc)_2.H_2O$ (0.5 equiv.), refluxing in MeOH/$CHCl_3$ (1:1), 4 h, 89%. R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$.

C–H), ν (C=O) of phenyl ester, ν (–C=N), ν (Ph) and ν (OPh) modes, respectively. The disappearance of the band 3416 cm^{-1} due to ν (OH) and shift of ν (–C=N) band to a lower frequency (1609 cm^{-1}), indicate bonding through azomethine nitrogen. The lowering in the ν (–C=N) band caused by the coordination of nitrogen to the metal center is in agreement with the result obtained for similar other complexes. The IR spectrum of nickel(II) complexes show absorption bands at (2928, 2862), 1720, 1611, (1574, 1514), and (1292, 1244) cm^{-1} which are assigned to ν (aliphatic C–H), ν (C=O) of phenyl ester, ν (–C=N), ν (Ph), and ν (OPh) modes, respectively. The disappearance of the band 3416 cm^{-1} due to ν (OH) and shift of ν (–C=N) band to a lower frequency (1609 cm^{-1}), indicate bonding through azomethine nitrogen. The proton NMR spectrum of bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoato] nickel(II) exhibits peaks at δ 8.24(s), 7.89–6.30(m), 3.98–3.92(t), 3.85(s), 1.78–1.27(m), and 0.87(t) ppm, which are assigned to –CH=N, ring, $–OCH_2$, $–COOCH_3$, $–[CH_2]_n$, and $–CH_3$ protons, respectively. The disappearance of the signal at 13.41 ppm (coordination via enolic oxygen atom) and the shift in the peak position

of the –CH=N signal in the complex (8.24 ppm) as compared to ligand (8.53 ppm), caused by decreased electron density due to donation of lone pair of electron from nitrogen atom to metal center, suggest coordination of ligand through the azomethine nitrogen.

The bands observed at 394, 311, and 257 nm in the electronic spectrum of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate are assigned to n–π^* and π–π^* transitions. In the spectrum of the bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino) benzoato]copper(II) complex, the bands are observed at 418, 378, 327, 304, and 249 nm. The first band is characteristic of square planar coordination around the metal center. The remaining bands are attributed to the π–π^* and n–π^* transitions of the ligand. The electronic spectrum of the orange colored nickel (II) complex shows transitions at 407, 392, 362, 311, and 278 nm. The first band is characteristic of square planar coordination around the metal centre and the remaining bands are attributed to the π–π^* and n–π^* transitions of the ligand.

3.2. DFT Study

The GAUSSIAN-03 program [21] package was employed to carry out DFT [22–27] calculations at the Becke's three parameter functional and Lee, Yang, and Parr correlation functional (B3LYP) level [28–30] of calculation and the 6–31G(d) basis set [31] was used for ground state geometry optimization and frequency calculations of the ligand. The internal coordinates of the system, which is used as input for GAUSSIAN-03 program was generated by the GAUSS VIEW 4.1 program [32]. The optimized structure of the ligand and its metal complex is given in Fig. 1.

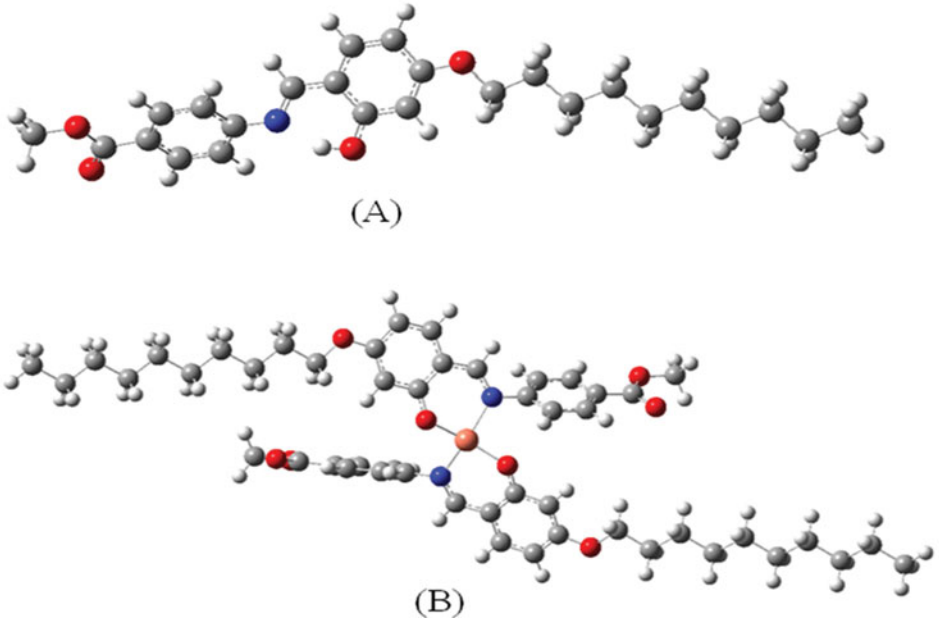


Figure 1. DFT optimized structure (ball and stick model) of (A) methyl 4-(4′-(decyloxy)-2 hydroxybenzylideneamino)benzoate; (B) Bis[methyl 4-(4′-(decyloxy)-2 hydroxybenzylideneamino)benzoato]copper(II) complex.

Table 1. Selected bond lengths and bond angles of Cu-complex of methyl 4-(4′-(decyloxy)-2 hydroxybenzylideneamino)benzoate in DFT optimized structure

Structure parameter	Cu-complex[a]
Cu–O(32)	1.920
Cu–O(87)	1.920
Cu–N(12)	2.036
Cu–N(77)	2.037
O(32)– Cu–O(87)	156.834
N(12)– Cu–N(77)	153.20
N(12)–Cu–O(87)	93.57
N(77)–Cu–O(32)	93.56
N(12)–Cu–O(32)	91.770
N(77)–Cu–O(87)	91.760

[a]Bond lengths are reported in angstrom (Å) and bond angles in degrees (°).

The absence of any imaginary frequencies in the calculated vibrational frequencies ensures that the optimized geometry corresponds to a true energy minimum. The length of fully extended ligand is found to be 27.47 Å, from DFT calculations. Some of the selective geometric parameters of optimized Cu(II) complex, evaluated by DFT calculation at B3LYP level, 631G(d) for ligand and LanL2DZ for metal are shown in Table 1.

The average Cu–O_{32} and Cu–N_{12} bond lengths of the complex are 1.92 and 2.036 Å, respectively, implying the presence of regular σ and dative bonding, respectively. The bond angles 156.83° and 153.20° for O_{32}–Cu–O_{87} and N_{12}–Cu–N_{77} respectively are around the copper atom. The bond angles are commensurate with square planar geometry around the metal ion.

3.3. Mesomorphic Behavior

The mesomorphic properties of methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino) benzoate and their copper(II) and nickel (II) complexes were characterized and investigated by DSC and POM. The phase transition temperature and thermodynamic data of the compounds are listed in Table 2.

The compound 1a showed endothermic peaks at 132.6°C, 140.2°C, and 145.9°C followed by the appearance of exothermic peaks at 142.13°C and 94.37°C. The three endothermic peaks observed for this compound define the crystal-to-crystal, crystal-to-mesophase, and mesophase-to-isotropic phase transition. The two exothermic peaks reveal an isotropic-to-mesophase and a mesophase-to-crystal phase transition. A Smectic A mesophase with focal conic texture is revealed for this compound in the heating and cooling cycle on the basis of POM. The texture of the mesophase is characteristic of a SmA mesophase, having a fluid property with higher viscosity and having stratified structures with well defined interlayer spacings. The interlayer attractions are weak and the layers are able to slide over one another relatively easily. The flexibility of the layers leads to distortions, which give rise to beautiful optical patterns known as the focal-conic texture (Fig. 2).

The molecules are aligned parallel to the layer normal, maintaining long range orientational ordering and short-range positional ordering, which lead to the SmA mesophase. A

Table 2. Transition temperature (T), transition enthalpy (ΔH), and transition entropy (ΔS) of methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino)benzoate and its copper(II) complex

		T, °C [ΔH, kJ/mol; ΔS, J/(mol K)]	
No	Compounds	Heating	Cooling
1	1.a	k′ 132.6 (18.79; 46.30) k″ 140.2 (24.9; 60.23) SmA 145.9 (4.01; 9.56) i	i 142.13 (−3.24; −7.80) SmA 94.37 (−24.21; −65.87) k
2	1.b	k′ 110.4 (12.19; 31.78) k″ 122.3 (31.69; 80.01) SmA 141.9 (3.71; 8.93) i	i 138.91 (−3.08; −7.74) SmA 97.79 (−27.69; −74.65) k
3	1.c	k′ 92.63 (8.79; 24.03) k″ 114.8 (27.69; 71.37) SmA 138.98 (2.76; 6.69) i	i 135.23 (−2.68; −6.56) SmA 99.25 (−29.48; −79.16) k′ 86.44 (8.76; 24.44) k″
4	1.d	k′ 106.14 (15.25; 40.20) k″ 115.39 (41.20; 106.03) SmA 139.35 (5.71; 13.84) i	i 137.55 (−5.58; −13.58) SmA 104.93 (−40.02; −105.85) k′ 99.69 (15.24; 40.87) k″
5	1.e	k 114.78 (50.81; 130.97) SmA 136.25 (3.19; 7.79) i	i 133.65 (−4.43; −10.88) SmA 106.48 (−53.45; −140.60) k′ 104.56 (− −) k″
6	1.f	k 122.34 (32.81; 81.36) SmA 132.1 (2.98; 7.35) i	i 128.59 (−4.01; −9.98) SmA 112.2 (−30.09; −78.08) k′ 106.15 (−14.78; −38.96) k″
7	2.a	k′ 126.34 (12.81; 32.06) k″ 225.12 (32.85; 65.92) SmA 232.14 (4.98; 9.80) i	i 220.17 (−1.86; −3.77) SmA 202.46 (−32.61; −68.56) k
8	2.b	k′ 124.18 (16.79; 42.25) k″ 216.73 (42.85; 87.47) SmA 223.81 (5.59; 11.24) i	i 215.63 (−3.21; −6.57) SmA 196.20 (−39.94; −85.09) k
9	2.c	k′ 118.60 (3.12; 26.30) k″ 191.92 (20.85; 108.63) SmA 208.21 (0.93; 1.93) i	i 204.21 (−0.86; −4.21) SmA 161.85 (−18.66; −115.29) k′ 117.18 (−1.41; −12.03) k″
10	2.d	k′ 123.09 (17.43; 43.98) k″ 203.27 (33.01; 69.28) SmA 224.23 (8.76; 17.61) i	i 213.25 (−2.11; −4.33) SmA 163.91 (−21.28; −48.68) k′ 116.26 (−10.45; −26.83) k″
11	2.e	k′ 119.09 (24.07; 61.36) k″ 200.61 (34.39; 72.60) SmA 217.63 (11.49; 23.41) i	i 208.71 (−5.01; −10.39) SmA 161.48 (−23.46; −53.97) k′ 110.78 (−6.97; −18.15) k″
12	2.f	k′ 128.23 (22.81; 56.82) k″ 198.31(29.21; 61.95) SmA 205.87 (6.85; 14.30) i	i 200.1 (−5.79; −12.23) SmA 197.10 (−27.19; −57.82) k′ 118.90 (−5.37; −13.69)k″

similar phase transition with a similar textural pattern is shown by compound 1b. The compound 1c showed endothermic peaks at 92.63°C, 114.8°C, and 138.98°C followed by the appearance of exothermic peaks at 135.23°C, 99.25°C, and 86.44°C. The three endothermic peaks observed for this compound define the crystal-to-crystal, crystal-to-mesophase, and mesophase-to-isotropic phase transition. The three exothermic peaks reveal an isotropic-to-mesophase transition, mesophase-to-crystal followed by the next crystal phase in the cooling cycle (Fig. 3).

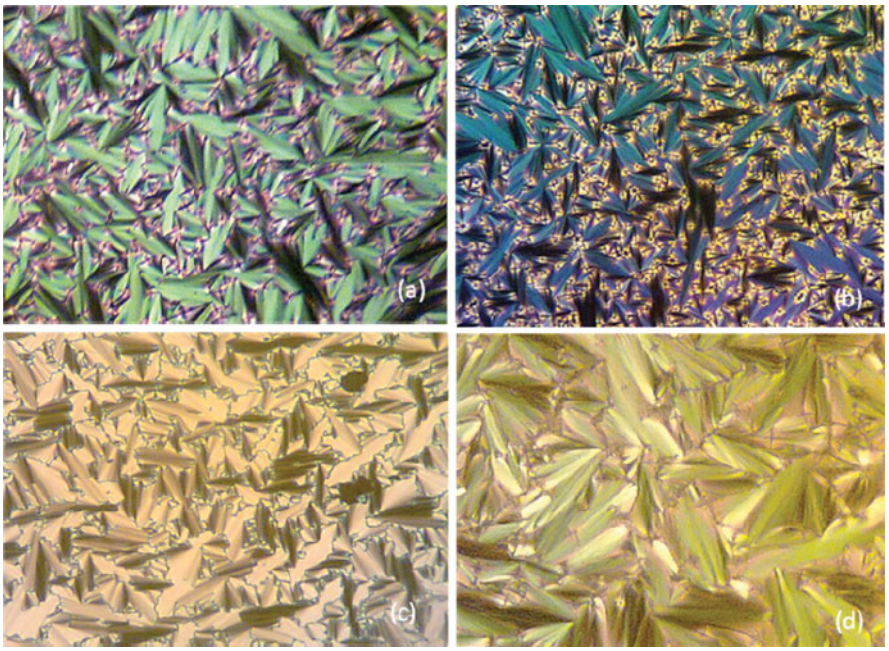


Figure 2. Optical textures of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate showing SmA mesophase under POM. (A) at 120°C (B) at 108°C and Optical textures of Bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino) benzoato]copper(II) showing SmA mesophase (C) at 180°C (D) at 200°C.

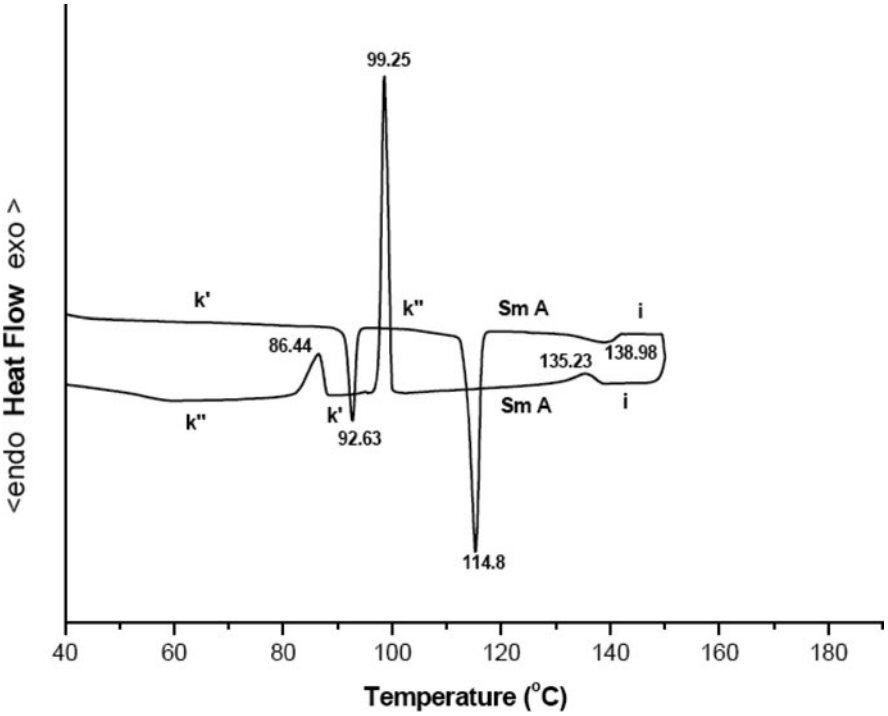


Figure 3. DSC thermogram of methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate.

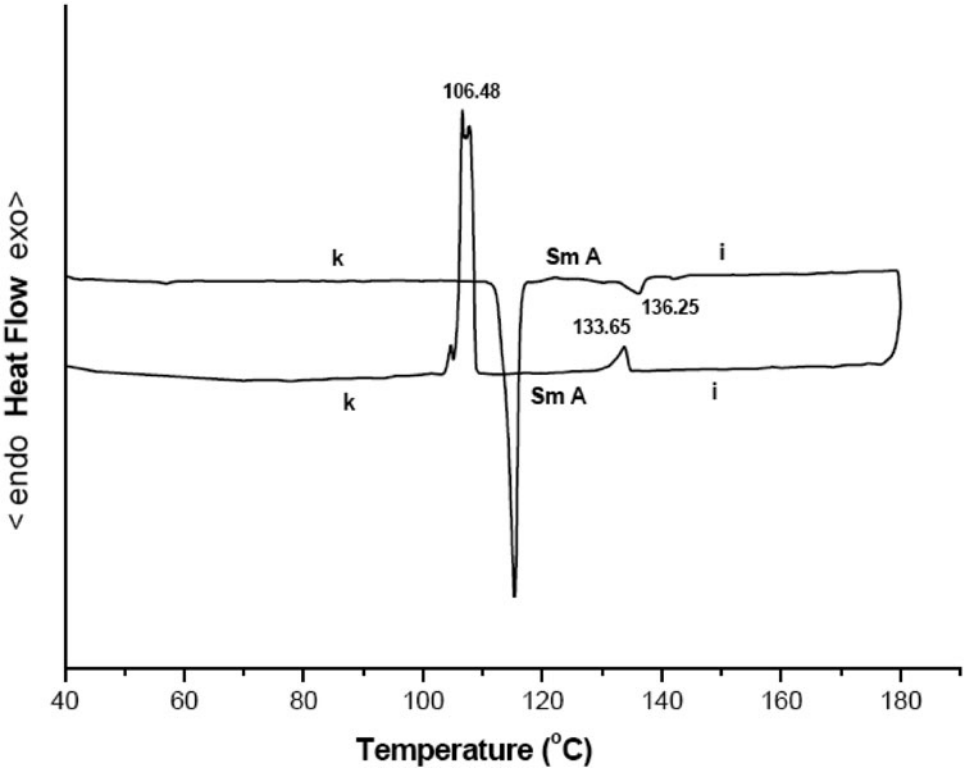


Figure 4. DSC thermogram of methyl 4-(4′-(tetradecyloxy)-2-hydroxybenzylideneamino)benzoate.

The similar phase behavior was obtained for the compound 1d. The compound 1e showed endothermic peaks at 114.78°C and 136.25°C followed by the appearance of exothermic peaks at 133.65°C, 106.48°C, and 104.56°C. The two endothermic peaks observed for this compound define crystal-to-mesophase and mesophase-to-isotropic phase transition. The three exothermic peaks reveal an isotropic-to-mesophase transition, mesophase-to-crystal followed by the next crystal phase in the cooling cycle (Fig. 4).

A similar phase transitions with a similar textural pattern is shown by compound 1f. All the ligands (1a–f) show enantiotropic SmA mesophase. Polymorphism based on the crystal-to-crystal phase transitions, is exhibited by compounds 1a–d in the heating cycle and 1c–f in cooling cycle.

The copper complexes of the series also exhibit SmA mesophase, but at higher temperature (above 190°C) in comparison to the parent ligands. The optical texture of the $(C_{10}L)_2Cu$ has been shown in Fig. 2. All the copper(II) complexes (2a–2e) show enantiotropic SmA mesophase. The compound 2a showed endothermic peaks at 126.34°C, 225.12°C, and 232.14°C followed by the appearance of exothermic peaks at 220.17°C and 202.46°C. The three endothermic peaks observed for this compound define the crystal-to-crystal, crystal-to-mesophase, and mesophase-to-isotropic phase transition. The two exothermic peaks reveal an isotropic-to-mesophase transition and mesophase-to-crystal transition. The similar phase behavior was obtained for the compound 2b. The compound 2c showed endothermic peaks at 118.60°C, 191.92°C, and 208.21°C followed by exothermic peaks at 204.21°C, 161.85°C, and 117.18°C. The three endothermic peaks observed for this compound define

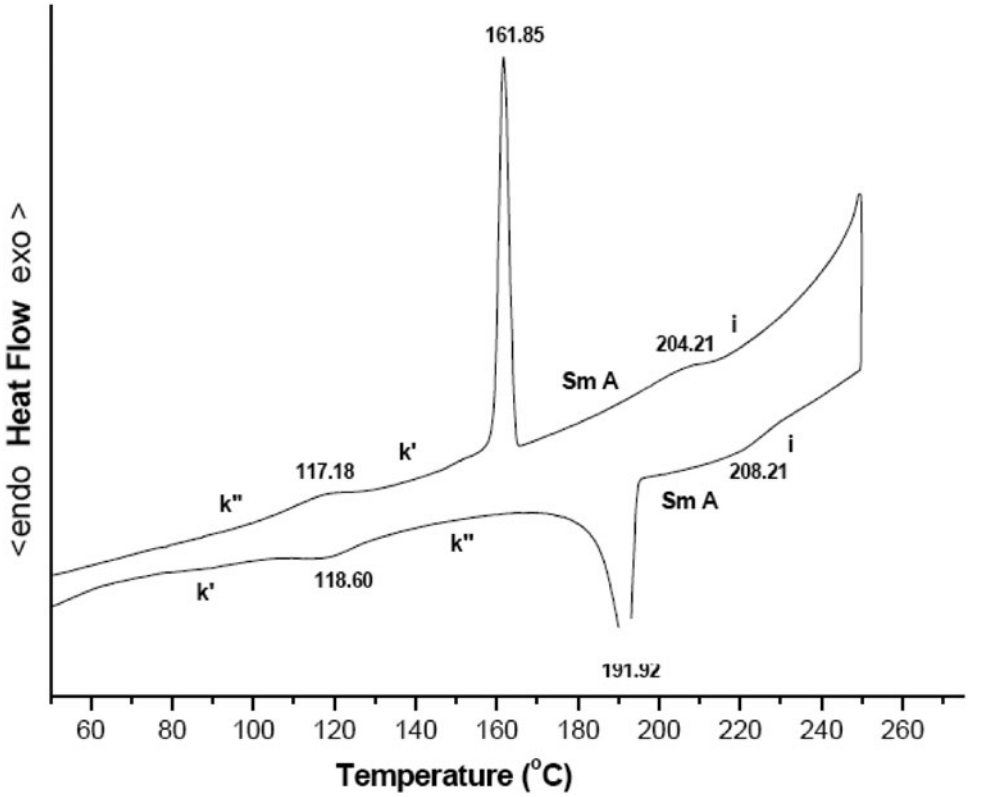


Figure 5. DSC thermogram of Bis[methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino) benzoato]copper(II) complex.

the crystal-to-crystal, crystal-to-mesophase, and mesophase-to-isotropic phase transition. The three exothermic peaks reveal an isotropic-to-mesophase and mesophase-to-crystal followed by the next crystal phase in the cooling cycle (Fig. 5).

A similar phase transition with a similar textural pattern is shown by compound 2d–f (Fig. 6). Polymorphism, based on the crystal-to-crystal phase transitions, is exhibited for compound 2a–f in the heating cycle and 2c–f in cooling cycle.

The nickel(II) complexes of methyl 4-(4′-(alkoxy)-2-hydroxybenzylideneamino) benzoate 3a–f were found to be nonmesogenic, with almost the same clearing temperature independent of the carbon chain length. The nonmesogenic nature of the nickel(II) complexes may be due to symmetrical and rigid geometry of the nickel complexes along with the stronger interaction of the potential donor (C═N) with the metal ion in the neighboring layers. This results in the decomposition of the molecules at higher temperature.

3.4. Thermo Gravimetric Analysis

Thermo gravimetric analyses of the mesogens indicate about their thermal stability, and for metal complexes along with thermal stability it also indicates about entrapping of solvents and coordination of water or solvents with metal ion as a coligand. The TGA of the mesogen methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate shows only 5% weight loss

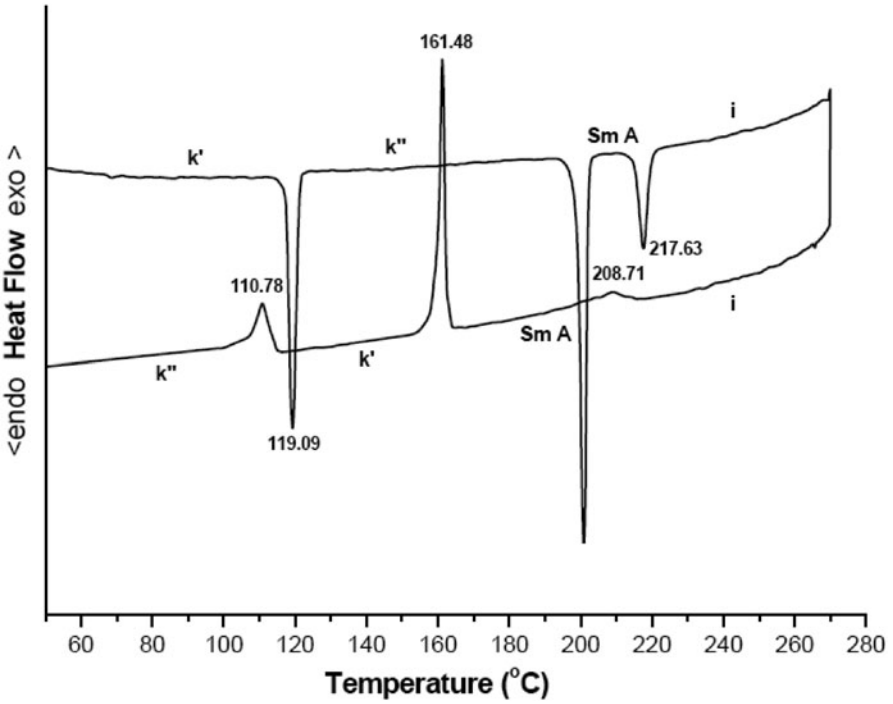


Figure 6. DSC thermogram of Bis[methyl 4-(4′-(tetradecyloxy)-2-hydroxybenzylideneamino) benzoato]copper(II) complex.

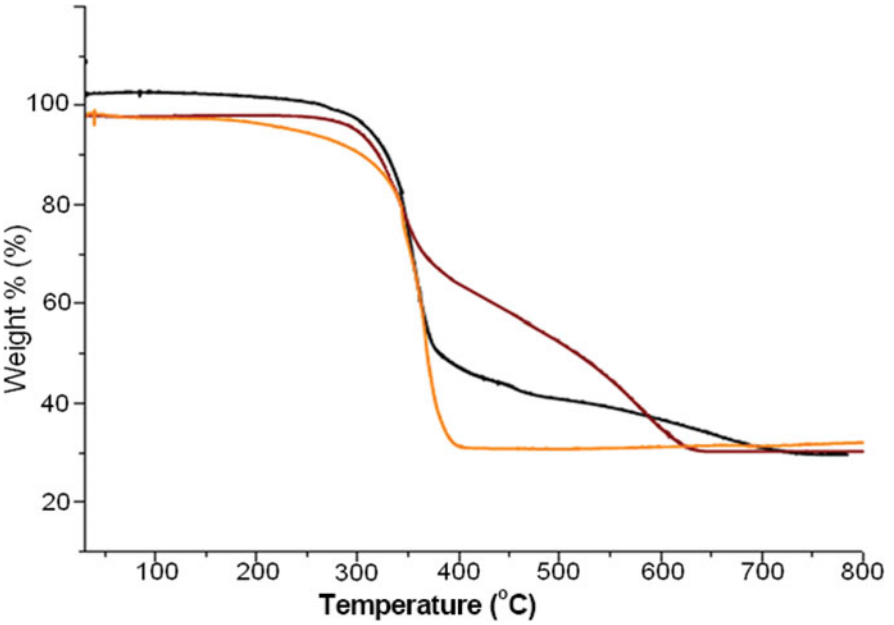


Figure 7. Thermal gravimetric analysis of mesogenic ligand methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate (black line) and its copper(II) (brown line) and nickel(II) complex (orange line).

from 100°C to 300°C and indicates good thermal stability of the mesogens. The TGA of the copper(II) complex shows no weight loss up to 300°C which indicates very good thermal stability of the complex. The TGA of the nickel(II) complexes shows no weight loss up to 200°C and decomposition temperature is found to be 342.5°C indicates that the nickel(II) complexes are also thermally stable. The TGA analysis indicates that no water or solvent is entrapped in the lattice or coordinated to the metal ion (Fig. 7).

4. Conclusions

A new series of mesogenic Schiff bases having a terminal alkoxy chain and a methyl benzoate as a polar end group and their copper(II) and nickel(II) complexes, have been synthesized and characterized. All the ligands and its copper (II) complexes show an enatiotropic SmA mesophase, but the nickel(II) complexes are nonmesogenic in nature. The methyl 4-(4′-(decyloxy)-2-hydroxybenzylideneamino)benzoate and its copper(II) and nickel(II) complexes show a high-thermal stability (above 300°C).

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