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Twin effects of induction and stabilization of SmA* phase by Cu(II) upon 4,4'-disubstituted salicylideneimine containing [1,2,3]-triazole and cholesterol arms

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Abstract

A new series of Cu(II) metallomesogen containing 4,4'-disubstituted salicyldeneimine armed with two mesogenic units of [1,2,3]-triazole and cholesterol were synthesized and characterized. Spectroscopic techniques such as UV-visible, FT-IR, ^{1}H-NMR and elemental analysis were employed to elucidate the molecular structures. The polarizing optical microscope (POM) and differential scanning calorimetry (DSC) have confirmed that all the complexes and ligands exhibited enantiotropic chiral mesophase. The ligand with terminal dodecanoate chain exhibited enantiotropic N* and SmC* phases, while the other homologous members with even alkanoate chain ranging from $C_{14}H_{29}$ to $C_{20}H_{41}$ exhibited exclusively SmC* phase only. Surprisingly, their corresponding Cu(II) complexes exhibited a new SmA* phase which was absent in their respective ligands. Comparison studies between the present compounds with earlier reported Cu(II) complexes have further uncovered that the incorporation of Cu(II) ion would increase the colinearity and the presence of N atom from [1,2,3]-triazole ring could increase the acentral transverse dipole and permanent dipole in between the molecules. As such it led to enhance the smectogenic properties. Besides, all the Cu(II) complexes reported in this study are thermally more stable than their corresponding ligands.

Keywords: Triazole, Cu(II) metallomesogens, SmC*, SmA*, Salicyldeneimine.

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1. Introduction

Liquid-crystal (LC) dimers formed by two structurally identical (symmetrical) or non-identical (unsymmetrical) mesogenic entities that are covalently connected through a flexible spacer have attracted much attention [1]. One of the reasons could be due to their poly-mesomorphism properties [1, 2]. There are notable differences in the liquid crystalline behaviors for unsymmetrical and symmetrical dimers. The symmetrical dimers exhibit monolayer smectic phase while the unsymmetrical LC dimers usually exhibit an intercalated smectic phase [3]. Their thermal and liquid crystalline properties are dependent on the length of the spacers, types of bridging group between the two aromatic rings and the terminal group attached to the aromatic ring [4].

Recently chiral dimers especially unsymmetrical dimers containing a cholesteryl ester unit which has covalently connected to different mesogenic moieties through a flexible spacer have been extensively studied [5]. This could be attributed to not only because cholesterol is wide spread in nature and commercially available, but also due to its unique properties originated from the chiral centre and helical conformation [5]. The cholesterol-based unsymmetrical dimers often exhibit various chiral mesophases including blue phase (BP), chiral nematic (N*), twist grain boundary (TGB) and chiral smectic C (SmC*) phases [4]. Among these, the BP which has three-dimensional cubic structures ranging between the chiral nematic and isotropic phases is well known for its potential in display industries [6]. The helical structures with respect to N*, SmC* and chiral smectic A (SmA*) phases have been widely applied in electro-optic storage devices [7, 8]. Among these chiral mesophase, the SmC* phase possesses the shortest switching time and could be used to develop fast response electro-optical devices [8, 9]. Besides, Gathania and co-worker discovered that the switching time of molecules in chiral mesophase decreased when temperatures were elevated [9].

The last decade has shown a steady increase in the interest towards liquid crystalline compounds containing five-membered heterocyclic rings [10]. One of the candidates categorized as [1,2,3]-triazole ring can be synthesized by click reaction which involves the copper catalysed [3 + 2] dipolar cycloaddition between an organic azides and terminal alkynes [10-14]. The wide spread usage of [1,2,3]-triazole as core units in the LC can be attributed to the ability of [1,2,3]-triazole heterocyclic rings to impart lateral and longitudinal dipoles have become the main reason for it to be widely used as core unit in thermotropic liquid crystals [10, 11]. In addition,

the high polarizability of nitrogen atom as compared to carbon may result in considerable changes in the physical properties of corresponding liquid crystalline phases [10, 11]. The non-linearity of [1,2,3]-triazole ring can give targeted compounds with lower melting points which entail the formation of different liquid crystalline mesophases [11]. Besides, the members from this class of material also exhibited good biological activities such as *b*-lactamase inhibitory, anti-HIV, anti-bacterial, anti-histamin, anti-tumor and anti-epileptic activities [15, 16, 17]. In the field of material chemistry, [1,2,3]-triazoles have been used as light stabilizers, fluorescent whiteners, optical brightening agents, corrosion inhibitors and photostabilizers for fibers, plastics or dyes [18].

Cu(II) containing mesogens, commonly known as metallomesogen, have received great attention leading to systematic research and development [19]. From the chemical and physical point of view, the central Cu(II) ions can enhance the ferroelectric properties, one-dimensional electrical conductivity, conversion of non-mesogenic ligands to mesogenic complexes [20-24]. Moreover, the resulting metal complexes are more polarizable and more suitably oriented for the fortification properties [22]. Besides, metallomesogens also possess different geometrical shapes, such as square planar, folder square, pyramidal and octahedral geometrical shape, which may not be obtained in conventional organic liquid crystals [25, 26].

Metallomesogenic molecules containing transition metal can increase the ratio of aromatic core to terminal flexible chain leading to the enhancement of the thermal stability of both crystal and liquid crystal phases [27]. Recently, the liquid crystalline compounds containing cholesterol group and [1,2,3]-triazole ring moieties have been reported by few different groups of researcher [7, 28, 29]. However, this type of compound has not been extensively studied especially in the field of metallomesogens. This has prompted us to prepare a new class of mesogenic complexes derived from [1,2,3]-triazole ring and cholesteryl 8-bromooctanoate units. These two units were covalently connected by salicyldeneimine fragment. This research forms the foundation for the investigation on the relationship between structure and property in [1,2,3]-triazole, cholesterol-based unsymmetrical dimesogenic bidentate ligands and their corresponding Cu(II) complexes.

2. Experimental

2.1 Chemicals and reagents

Cholesterol, 8-bromooctanoic acid and sodium ascorbate, 4-nitroaniline, 4-dimethylaminopyridine (DMAP) and propargyl alcohol were purchased from Sigma Aldrich. Whilst 2,4-dihydroxybenzaldehyden and *N,N′*-dicyclohexylcarbodiimide (DCC) were obtained from TCI (Tokyo Chemical Industry), copper(II) sulphate pentahydrate, copper(II) acetate dehydrate and sodium azide were acquired from Qrec-Chemicals. On the other hands, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid and iron powders were purchased from Merck. Sodium nitrite and ammonium chloride were acquired from R&M chemicals. All the chemicals as well as solvents were purchased commercially and used directly from the bottles without further purification.

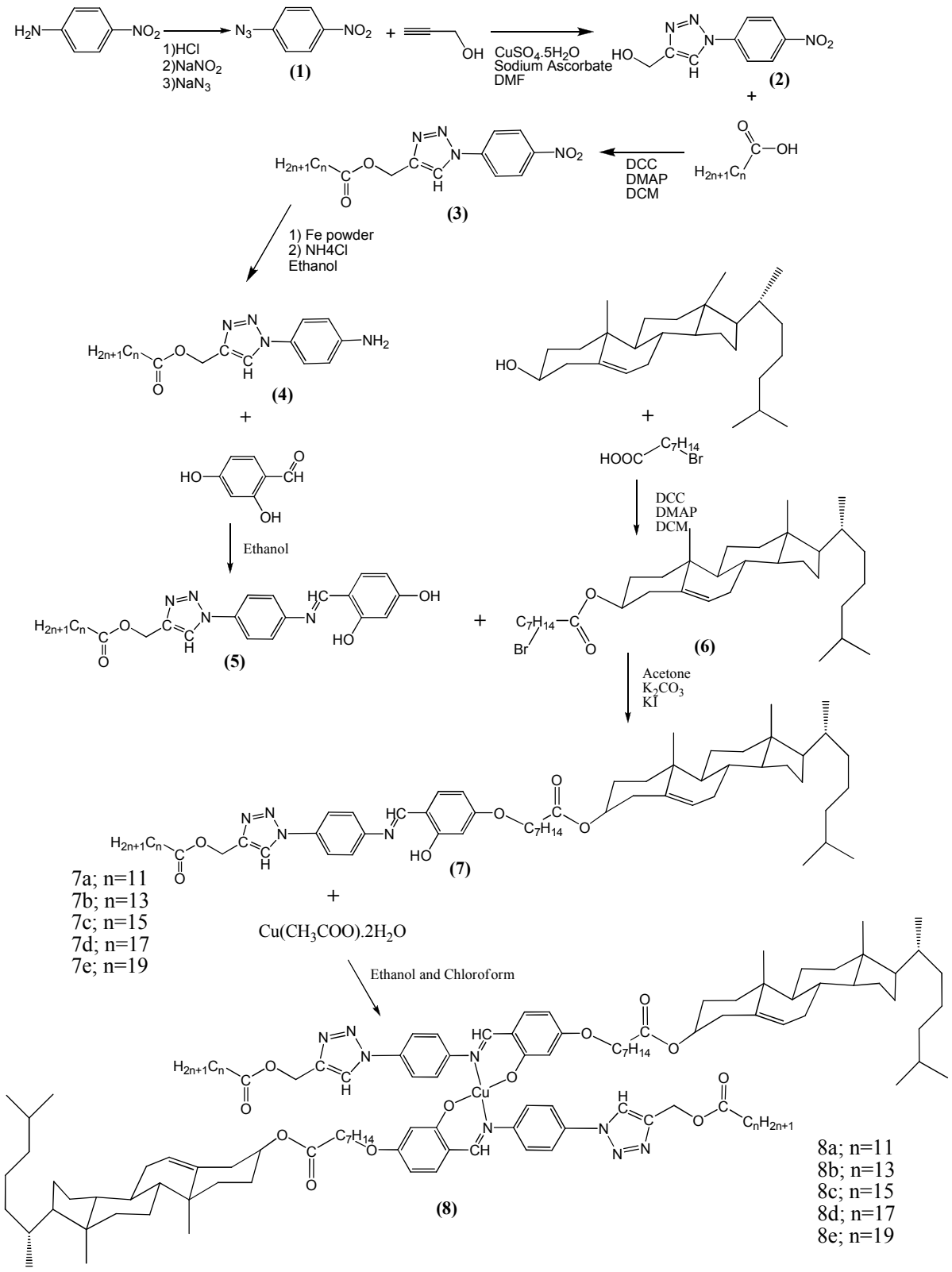
2.2 Physical measurement

The proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured by Bruker Avance 500 MHz ultrashield spectrometers equipped with ultrashield magnets. Deuterated chloroform ($CDCl_3$) and dimethysulphoxide (DMSO-d_6) were used as solvent and TMS as internal standard. The fourier transform infrared (FT-IR) spectra were acquired from Perkin Elmer 2000-FTIR spectrophotometer in the frequency range 4000-400cm^{-1} with sample embedded in KBr discs. The elemental (C, H and N) analysis was carried out using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Perkin Elmer Lambda 25 UV/Vis spectrometer was used to record UV-visible spectra. Thin layer chromatography was performed with TLC sheets coated with silica and spots were detected by UV irradiation. Differential scanning calorimetry (DSC) thermographs were measured by a Seiko DSC6200R calorimeter with the heating and cooling rate of ±5^{o}C. The thermal-optical observations and microphotographs of all compounds were observed by Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam LTS 350 hot stage and TMS94 temperature controller.

2.3 Synthesis

A homologous series of [1,2,3]-triazole, cholesterol-based dimesogenic Schiff bases ligands and their corresponding Cu(II) complexes were synthesized for their mesomorphic and thermal properties studies. Scheme 1 shows the synthetic route for the dimesogenic Schiff bases ligands **7a-7e** and their corresponding Cu(II) complexes **8a-8e**. The conversion of 4-nitroaniline to azido-4-nitrobenzene was conducted by using concentrated hydrochloric acid, sodium nitrite

and sodium azide as reaction reagents. The intermediate **1** then underwent Cu(I) catalyzed "click reaction" with propagyl alcohol to yield the targeted [1,2,3]-triazole ring intermediate **2.** The triazole intermediate thus obtained was subjected to steglich esterification with even parity of fatty acid. The reduction of nitro to amine functional group in intermediates **4** were carried out using iron powder and ammonium chloride as reagents. The intermediates **5** were prepared by the condensation reaction of intermediates **4** with 2,4-dihydroxybenzaldehyde which was followed by the Williamson etherification with cholesterly 8-bromooctanoate, which in turn was prepared by steglic esterification of commercial cholesterol with 9-bromononanoic acid . Finally, the synthesized ligands **7** were reacted with Cu(II) acetate dihydrate to afford the desired Cu(II) complexes **8**. The chemical structures for all the intermediates, targeted ligands and Cu(II) complexes were elucidated by FT-IR, ^{1}H-NMR, UV-visible spectrometer and elemental analysis. The codes for ligands **7** and their corresponding Cu(II) complexes **8** with various alkanoate groups of even parity (n= 12-20) were given in Scheme **1.**



Scheme 1: Synthetic routes toward formation of **7a-7e** and their corresponding Cu(II) complexes **8a-8e**.

*2.3.1 Synthesis of intermediate **1***

First, 4-nitroaniline (8g, 57mmol) was dissolved in concentrated hydrochloric acid in a 250 ml round bottom flask under magnetic stirring. Sodium nitrate (5.99g, 37mmol) which has been dissolved in distilled water was added dropwise into the solution. Then, sodium azide (5.65g, 86mmol) in distilled water was added dropwise to the diazodium salt solution under vigorous stirring. The resulting solution was allowed to stir at 0 ^{o}C by using ice bath for 1 hour. Finally, the obtained mixture was extracted several times with chloroform and water. The extracted solution was evaporated at room temperature to give the yellow pure product.

*2.3.2 Synthesis of intermediate **2***

Intermediate **1** (6g, 36mmol) and propagyl alcohol (4.10g, 73mmol) were dissolved in DMF in a two neck round bottom flask. The mixture was then treated with 20-mole % of $Cu.SO_4.5H_2O$ in DMF which was followed by 20-mole % sodium ascorbate in minimum amount of water. The reaction mixture was stirred at room temperature for 24 hours and then poured into ice water. The resulting precipitate was obtained by suction filtration and recrystallized several times from ethanol to yield the pure orange precipitate.

*2.3.3 Synthesis of intermediate **3***

Intermediate **2** (2 mmol) in dichloromethane (DCM) was added into a mixture of fatty acid (2 mmol) and dicyclohexylcarbodiimide, DCC (2 mmol) which has been dissolved in DCM in a round bottom flask. Dimethylaminopyridine (0.2 mmol), DMAP in DCM was then added dropwise into the mixture while stirring at room temperature. The reaction was stirred overnight and the mixture was filtered. The filtrate thus obtained was evaporated at room temperature to remove the solvent. The product was recrystallized twice from ethanol.

*2.3.4 Synthesis of intermediate **4***

Intermediate **3** (10mmol) in ethanol solvent in a round bottom flask was heated until it dissolved. Iron powder (60mmol) was added and followed by ammonium chloride in minimum amount of water. The resulting mixture was refluxed under stirring for 6 hours. The mixture was then cooled to room temperature and filtered. Water was added to the filtrate and extracted

several times by using ethyl acetate. The extracted solution was evaporated at room temperature to give the pure precipitate**.**

*2.3.5 Synthesis of intermediate **5***

An equivalent amount (10mmol) of 2,4-dihydroxybenzaldehyde and intermediate **4**, along with catalytic amount of acetic acid were mixed in ethanol and refluxed for 6 hours. The mixture was then concentrated by evaporating out the ethanol at room temperature and the precipitate thus obtained was recrystallized from ethanol to yield the desired product.

*2.3.6 Synthesis of intermediate **6***

Cholesterol (3g, 7.7mmol) dissolved in dichloromethane (DCM) was treated with dicyclohexylcarbodiimide, DCC (1.6g, 7.7mmol) which followed by 8-bromooctanoic acid (1.7g, 7.7mmol). Dimethylaminopyridine, DMAP (0.19g, 1.5mmol) was added and the mixture was stirred at room temperature for overnight. The dicyclohexylurea thus formed was removed by filtration and the filtrate was concentrated under room temperature. The resulting white precipitate was purified several time by recrystallization from ethanol.

2.3.7 Synthesis of [1,2,3]-triazole, cholesterol-based dimesogenic Schiff bases ligands, 7

To a mixture containing equimolar of cholestery 8-bromooctanoate and intermediate **5** in acetone, one equivalent of potassium carbonate and catalytic amount of potassium iodine were added. The reaction mixture was heated for overnight at 60 ^{o}C and then filtered to get rid of the potassium carbonate and potassium iodine. The obtained filtrate was evaporated to dryness and the precipitate thus obtained was washed with distilled water. The yellow product was then dried and recrystallized from ethanol.

The percentage yields and analytical datas for ligands **7** are summarized as below:

7a: yellow, yield 43%. Elemental analysis/% : Found C 75.62, H 9.50, N 5.53; calculated ($C_{64}H_{96}N_4O_6$), C 75.55, H 9.51, N 5.51;. IR (KBr) ν_{max}/cm^{-1}: 1172 (C-O ether), 1297 (C-O phenolic), 1598 (C=C), 1626 (C=N), 1733 (C=O ester), 2932-2851 (C-H alkyl), 3429 (O-H). ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.60 (s, 3H, CH_3), δ 0.78-1.92 (m, 71H, aliphatic and cholesteric protons), δ 2.21-2.28 (m, 6H, CH_2), δ 3.94 (t, 2H, OCH_2), δ 4.54-4.56 (m, 1H, OCH), δ 5.24 (s, 2H, OCH_2), δ 5.20 (br, d, 1H, C=CH), δ 6.45 (d, 1H, Ar-H), δ 6.49 (s, 1H, Ar-H), δ

7.23 (d, 1H, Ar-H), δ 7.34 (d, 2H, Ar-H), δ 7.71 (d, 2H, Ar-H), δ 7.98 (s, 1H, N-CH), 8.49 (s, 1H, N=CH), 13.26 (br, s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.2-57.1 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 57.4, δ 68.9 (O<u>C</u>H$_2$), δ 74.1 (<u>C</u>-O), δ 102.0, δ 108.44, δ 112.7, δ 121.9, δ 122.6, δ 134.3, δ 135.5, δ 149.1, δ 163.8, δ 164.0 ($C_{aromatic}$), δ 122.9 (C=<u>C</u>H$_{cholesteric}$), δ 122.1, δ 140.0 ($C_{triazole}$), δ 140.1 (<u>C</u>=CH$_{cholesteric}$), δ 162.1 (H<u>C</u>=N), δ 173.5, δ 173.8 (<u>C</u>=O).

7b: yellow, yield 56%. Elemental analysis/% : Found C 75.99, H 9.69, N 5.37; calculated ($C_{66}H_{100}N_4O_6$), C 75.82, H 9.64, N 5.36;. IR (KBr) ν_{max}/cm^{-1}: 1172 (C-O ether), 1297 (C-O phenolic), 1598 (C=C), 1627 (C=N), 1733 (C=O ester), 2931-2850 (C-H alkyl), 3429 (O-H). ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.60 (s, 3H, CH_3), δ 0.78-1.92 (m, 75H, aliphatic and cholesteric protons), δ 2.20-2.27 (m, 6H, CH_2), δ 3.94 (t, 2H, OCH_2), δ 4.54-4.56 (m, 1H, OCH), δ 5.23 (s, 2H, OCH_2), δ 5.20 (br, d, 1H, C=CH), δ 6.45 (d, 1H, Ar-H), δ 6.48 (s, 1H, Ar-H), δ 7.23 (d, 1H, Ar-H), δ 7.35 (d, 2H, Ar-H), δ 7.71 (d, 2H, Ar-H), δ 7.98 (s, 1H, N-CH), 8.49 (s, 1H, N=CH), 13.26 (br, s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.1-57.0 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 57.3, δ 68.9 (O<u>C</u>H$_2$), δ 74.1 (<u>C</u>-O), δ 102.1, δ 108.44, δ 112.6, δ 121.9, δ 122.6, δ 134.3, δ 135.5, δ 149.2, δ 163.8, δ 164.1 ($C_{aromatic}$), δ 122.9 (C=<u>C</u>H$_{cholesteric}$), δ 122.1, δ 140.0 ($C_{triazole}$), δ 140.0 (<u>C</u>=CH$_{cholesteric}$), δ 162.1 (H<u>C</u>=N), δ 173.5, δ 173.8 (<u>C</u>=O).

7c: yellow, yield 63%. Elemental analysis/% : Found C 76.31, H 9.79, N 5.28; calculated ($C_{68}H_{104}N_4O_6$), C 76.08, H 9.76, N 5.22;. IR (KBr) ν_{max}/cm^{-1}: 1172 (C-O ether), 1297 (C-O phenolic), 1599 (C=C), 1626 (C=N), 1734 (C=O ester), 2932-2851 (C-H alkyl), 3429 (O-H). ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.61 (s, 3H, CH_3), δ 0.78-1.92 (m, 79H, aliphatic and cholesteric protons), δ 2.21-2.28 (m, 6H, CH_2), δ 3.95 (t, 2H, OCH_2), δ 4.54-4.56 (m, 1H, OCH), δ 5.24 (s, 2H, OCH_2), δ 5.20 (br, d, 1H, C=CH), δ 6.44 (d, 1H, Ar-H), δ 6.49 (s, 1H, Ar-H), δ 7.24 (d, 1H, Ar-H), δ 7.34 (d, 2H, Ar-H), δ 7.72 (d, 2H, Ar-H), δ 7.98 (s, 1H, N-CH), 8.49 (s, 1H, N=CH), 13.26 (br, s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.2-57.1 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 57.4, δ 68.9 (O<u>C</u>H$_2$), δ 74.1 (<u>C</u>-O), δ 102.0, δ 108.44, δ 112.7, δ 121.9, δ 122.6, δ 134.3, δ 135.6, δ 149.1, δ 163.7, δ 164.0 ($C_{aromatic}$), δ 122.9 (C=<u>C</u>H$_{cholesteric}$), δ 122.0, δ 140.0 ($C_{triazole}$), δ 140.2 (<u>C</u>=CH$_{cholesteric}$), δ 162.2 (H<u>C</u>=N), δ 173.5, δ 173.8 (<u>C</u>=O).

7d: yellow, yield 48%. Elemental analysis/% : Found C 76.31, H 9.89, N 5.08; calculated ($C_{70}H_{108}N_4O_6$), C 76.32, H 9.88, N 5.09;. IR (KBr) ν_{max}/cm^{-1}: 1172 (C-O ether), 1296 (C-O phenolic), 1598 (C=C), 1626 (C=N), 1734 (C=O ester), 2932-2851 (C-H alkyl), 3429 (O-H). ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.60 (s, 3H, CH_3), δ 0.78-1.92 (m, 83H, aliphatic and cholesteric protons), δ 2.21-2.28 (m, 6H, CH_2), δ 3.95 (t, 2H, OCH_2), δ 4.54-4.56 (m, 1H, OCH), δ 5.24 (s, 2H, OCH_2), δ 5.21 (br, d, 1H, C=CH), δ 6.44 (d, 1H, Ar-H), δ 6.48 (s, 1H, Ar-H), δ 7.24 (d, 1H, Ar-H), δ 7.34 (d, 2H, Ar-H), δ 7.72 (d, 2H, Ar-H), δ 7.98 (s, 1H, N-CH), 8.49 (s, 1H, N=CH), 13.27 (br, s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.1-57.1 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 57.5, δ 68.9 (O<u>C</u>H_2), δ 74.1 (<u>C</u>-O), δ 102.0, δ 108.44, δ 112.7, δ 121.9, δ 122.6, δ 134.2, δ 135.4, δ 149.1, δ 163.8, δ 164.0 ($C_{aromatic}$), δ 122.9 (C=<u>C</u>$H_{cholesteric}$), δ 122.0, δ 140.0 ($C_{triazole}$), δ 140.1 (<u>C</u>=$CH_{cholesteric}$), δ 162.2 (H<u>C</u>=N), δ 173.5, δ 173.8 (<u>C</u>=O).

7e: yellow, yield 59%. Elemental analysis/% : Found C 76.88, H 10.07, N 4.98; calculated ($C_{72}H_{112}N_4O_6$), C 76.55, H 9.99, N 4.96;. IR (KBr) ν_{max}/cm^{-1}: 1171 (C-O ether), 1297 (C-O phenolic), 1598 (C=C), 1626 (C=N), 1734 (C=O ester), 2931-2850 (C-H alkyl), 3430 (O-H). ^{1}H NMR (500 MHz, $CDCl_3$), δ/ppm: δ 0.62 (s, 3H, CH_3), δ 0.78-1.92 (m, 83H, aliphatic and cholesteric protons), δ 2.22-2.28 (m, 6H, CH_2), δ 3.95 (t, 2H, OCH_2), δ 4.53-4.55 (m, 1H, OCH), δ 5.24 (s, 2H, OCH_2), δ 5.21 (br, d, 1H, C=CH), δ 6.44 (d, 1H, Ar-H), δ 6.49 (s, 1H, Ar-H), δ 7.24 (d, 1H, Ar-H), δ 7.34 (d, 2H, Ar-H), δ 7.72 (d, 2H, Ar-H), δ 7.98 (s, 1H, N-CH), 8.49 (s, 1H, N=CH), 13.27 (br, s, 1H, Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ/ppm: δ 12.2-57.1 ($C_{aliphatic}$ and $C_{cholesteric}$), δ 57.3, δ 68.9 (O<u>C</u>H_2), δ 74.1 (<u>C</u>-O), δ 102.0, δ 108.44, δ 112.6, δ 121.9, δ 122.6, δ 134.3, δ 135.4, δ 149.1, δ 163.8, δ 164.1 ($C_{aromatic}$), δ 122.9 (C=<u>C</u>$H_{cholesteric}$), δ 122.1, δ 140.0 ($C_{triazole}$), δ 140.1 (<u>C</u>=$CH_{cholesteric}$), δ 162.0 (H<u>C</u>=N), δ 173.5, δ 173.7 (<u>C</u>=O).

2.3.8 Synthesis of copper(II) complexes ***8***

Dimesogenic Schiff bases ligands 7 (10mmol) was heated in a solvent mixture of ethanol and chloroform. Copper(II) acetate dihydrate (5mmol) was dissolved in hot ethanol and added dropwise. The mixture was stirred and refluxed for 5 hours. After cooled to room temperature, the light brown precipitate of complex **8** was filtered off, washed several time with hot ethanol and recrystallized from chloroform-ethanol (1:1) sovent.

The percentage yields and analytical datas for complexes **8** are summarized as below:

8a: light brown, yield 89%. Elemental analysis/% : Found C 73.38, H 9.14, N 5.33; calculated ($C_{128}H_{190}CuN_8O_{12}$), C 73.33, H 9.13, N 5.34;. IR (KBr) ν_{max}/cm^{-1}: 1173 (C-O ether), 1314 (C-O phenolic), 1598 (C=C), 1611 (C=N), 1734 (C=O ester), 2926-2852 (C-H alkyl).

8b: light brown, yield 83%. Elemental analysis/% : Found C 73.69, H 9.29, N 5.19; calculated ($C_{132}H_{198}CuN_8O_{12}$), C 73.65, H 9.27, N 5.21;. IR (KBr) ν_{max}/cm^{-1}: 1173 (C-O ether), 1315 (C-O phenolic), 1598 (C=C), 1610 (C=N), 1734 (C=O ester), 2926-2852 (C-H alkyl).

8c: light brown, yield 86%. Elemental analysis/% : Found C 74.08, H 9.46, N 5.09; calculated ($C_{136}H_{206}CuN_8O_{12}$), C 73.96, H 9.40, N 5.07;. IR (KBr) ν_{max}/cm^{-1}: 1172 (C-O ether), 1314 (C-O phenolic), 1598 (C=C), 1611 (C=N), 1734 (C=O ester), 2928-2852 (C-H alkyl).

8d: light brown, yield 79%. Elemental analysis/% : Found C 74.34, H 9.53, N 4.98; calculated ($C_{140}H_{214}CuN_8O_{12}$), C 74.25, H 9.52, N 4.95;. IR (KBr) ν_{max}/cm^{-1}: 1173 (C-O ether), 1315 (C-O phenolic), 1598 (C=C), 1610 (C=N), 1734 (C=O ester), 2926-2852 (C-H alkyl).

8e: light brown, yield 87%. Elemental analysis/% : Found C 74.78, H 9.69, N 4.87; calculated ($C_{144}H_{222}CuN_8O_{12}$), C 74.52, H 9.64, N 4.83;. IR (KBr) ν_{max}/cm^{-1}: 1173 (C-O ether), 1314 (C-O phenolic), 1598 (C=C), 1611 (C=N), 1734 (C=O ester), 2926-2852 (C-H alkyl).

3. Result and discussion

3.1 Mesomorphic properties

The CHN microanalysis, FT-IR and UV-visible spectra for Cu(II) complexes **8a-8e** and their corresponding ligands **7a-7e** are available in electronic supporting information. The mesophase texture, transition temperature and associated entropy changes for ligands **7** and their corresponding Cu(II) complexes **8** are listed in Tables 1 and 2. All homologous compounds are enantiotropic and exhibit chiral mesophase. The unsymmetrical dimesogenic ligand **7a** possessing terminal with even parity $C_{12}H_{25}$ exhibits enantiotropic chiral nematic phase (N*) and chiral smectic C phase (SmC*). The N* phase is confirmed on the basis of the observation of oily streak texture (Figure 1) during heating process and a focal-conic fan texture (Figure 2) during the cooling process from isotropic phase [30-33]. The focal-conic fan texture subjected to mechanical shearing is easily transformed to an oily streak texture (Figure 1). This observation further indicates the presence of N* phase. Upon further cooling, the N* phase is transformed to SmC* which is indicated by the existence of chiral line on top of the focal-conic fan texture

(Figure 3) [6, 32]. Elongation of the terminal chain with even parity from $C_{14}H_{28}$ to $C_{20}H_{41}$ in ligands **7b-7e** caused the suppression of N* phase and showed predominantly SmC* phase. This phenomenon can be caused by the long terminal even parity in ligands **7c-7e** favoring the intermolecular interaction and intertwining, which in turn facilitate the lamellar packing causing the formation of SmC* phase only [34, 35]. The battonets with chiral line for ligands **7b-7e** in Figure 4 coalesce to form the SmC* phase (Figure 3).

Table 1: Phase transition temperature (^{o}C), entropy ($\Delta S/R$) and associated enthalpies (kJ/mol) of ligands **7.**

Ligands		Cr_1	Cr_2	SmC*	N*	I	$\Delta S_{SmC,I}/R$	$\Delta S_{N,I}/R$
7a	Heating	• 142.9 (33.6)		• 166.0[a]	• 171.3 (9.8)	•		3.3
	Cooling	• 127.3 (-31.0)		• 159.4[a]	• 169.6 (-9.4)	•		2.7
7b	Heating	• 127.7 (28.7)		•	162.7 (10.2)	•	2.8	
	Cooling	• 119.8 (-26.3)		•	158.9 (-9.7)	•	2.7	
7c	Heating	• 63.2 (12.0)	• 145.7 (63.4)	•	164.9 (12.0)	•	3.3	
	Cooling	• 58.1 (-6.7)	• 123.8 (-31.3)	•	163.3 (-11.6)	•	3.2	
7d	Heating	• 69.1 (14.9)	• 121.2 (29.4)	•	161.6 (13.4)	•	3.7	
	Cooling	• 74.4 (-5.6)	• 116.6 (-26.9)	•	156.3 (-12.9)	•	3.6	
7e	Heating	• 93.6 (8.8)	• 121.8 (28.0)	•	158.0[a]	•		
	Cooling	• 92.4 (-11.0)	• 117.0 (-26.1)	•	155.9[a]	•		

Cr_1, crystal 1; Cr_2, crystal 2 ; SmC*, chiral smectic C; N*, chiral nematic; I, isotropic.
[a]denotes transition temperature derived from polarising optical microscope equipped with hot stage

Table 2: Phase transition temperature (^{o}C), entropy ($\Delta S/R$) and associated enthalpies (kJ/mol) of Cu(II) complexes **8**.

Complex		Cr		SmC*		SmA*		I	$\Delta S_{SmA,I}/R$
8a	Heating	•	173.6 (71.5)	•	184.1[a]	•	195.5 (12.8)	•	3.3
	Cooling	•	116.8 (-21.1)	•	175.1[a]	•	190.3 (-10.5)	•	2.7
8b	Heating	•	167.9 (63.9)	•	179.7[a]	•	194.7 (9.3)	•	2.4
	Cooling	•	158.8 (-15.5)	•	167.8[a]	•	188.0 (-5.8)	•	1.5
8c	Heating	•	173.2 (65.8)	•	185.2[a]	•	195.5 (10.1)	•	2.5
	Cooling	•	104.4 (-16.6)	•	173.7[a]	•	189.7 (-6.63)	•	1.7
8d	Heating	•	162.9 (56.4)	•	177.6[a]	•	196.8 (14.1)	•	3.6
	Cooling	•	130.9 (-13.9)	•	166.7[a]	•	191.6 (-7.8)	•	2.0
8e	Heating	•	165.1 (57.2)	•	181.3[a]	•	197.4 (15.6)	•	3.9
	Cooling	•	146.4 (-19.9)	•	172.4[a]	•	192.1 (-13.2)	•	3.4

Cr_1, crystal 1; Cr_2, crystal 2 ; SmC*, chiral smectic C; SmA*, chiral smectic A; I, isotropic.
[a]denotes transition temperature derived from polarising optical microscope equipped with hot stage

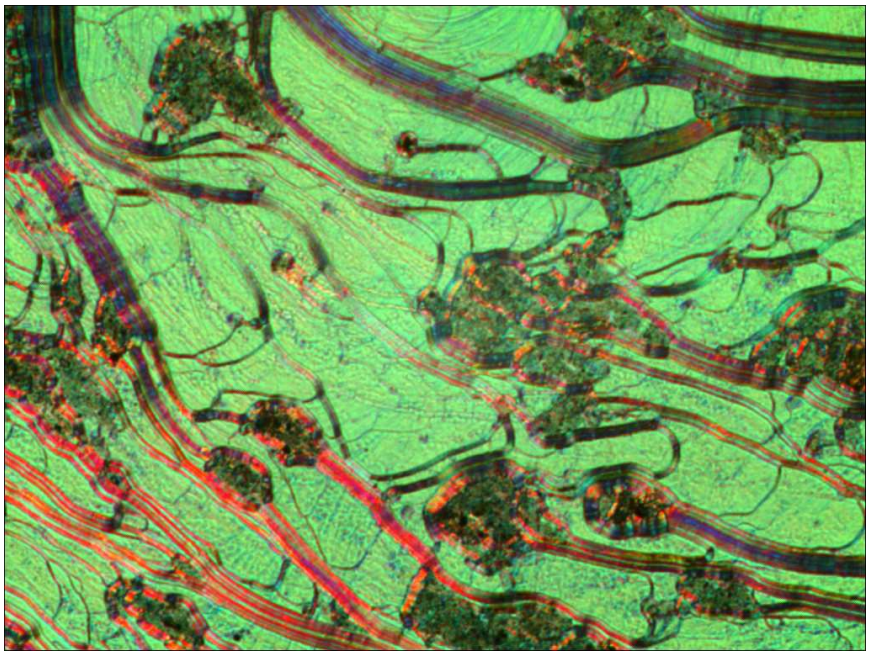


Figure 1: Photomicrograph showing oily streak texture of N* phase of ligands **7a** at 169.0 ^{o}C upon heating**.**

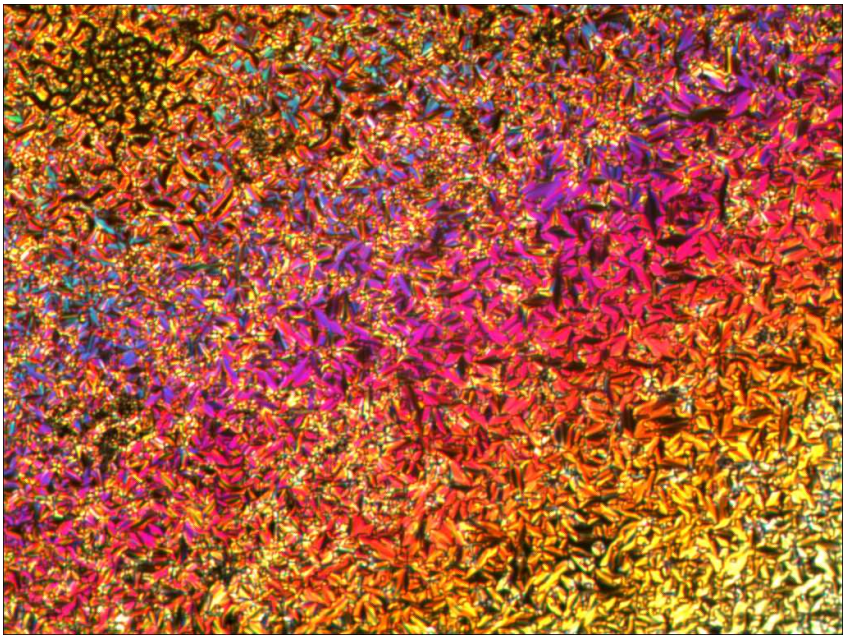


Figure 2: Photomicrograph showing focal-conic fan texture of N* phase of ligands **7a** at 158.0 ^{o}C upon cooling

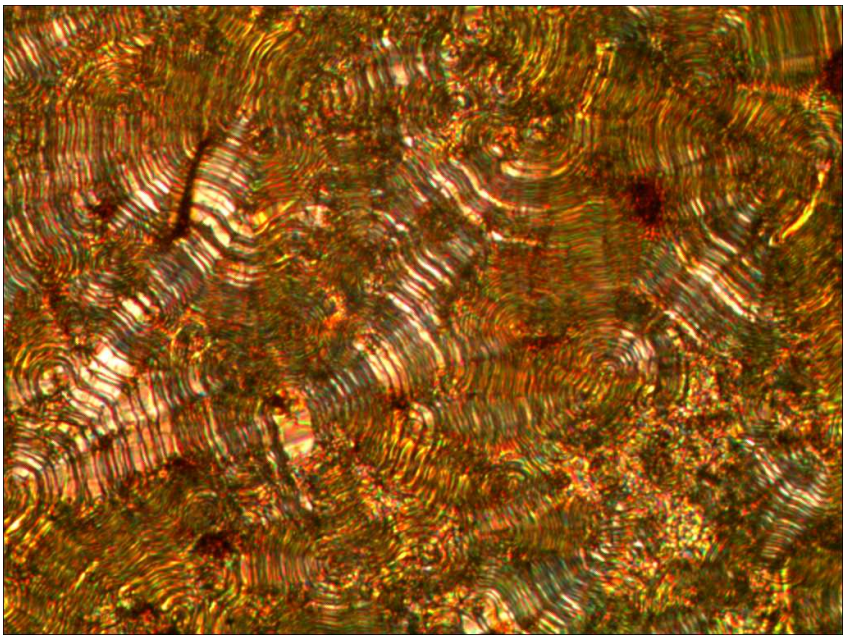


Figure 3: Photomicrograph showing the presence of chiral line on focal-conic fan texture of SmC* phase of ligands **7a** at 131.0 ^{o}C upon cooling.

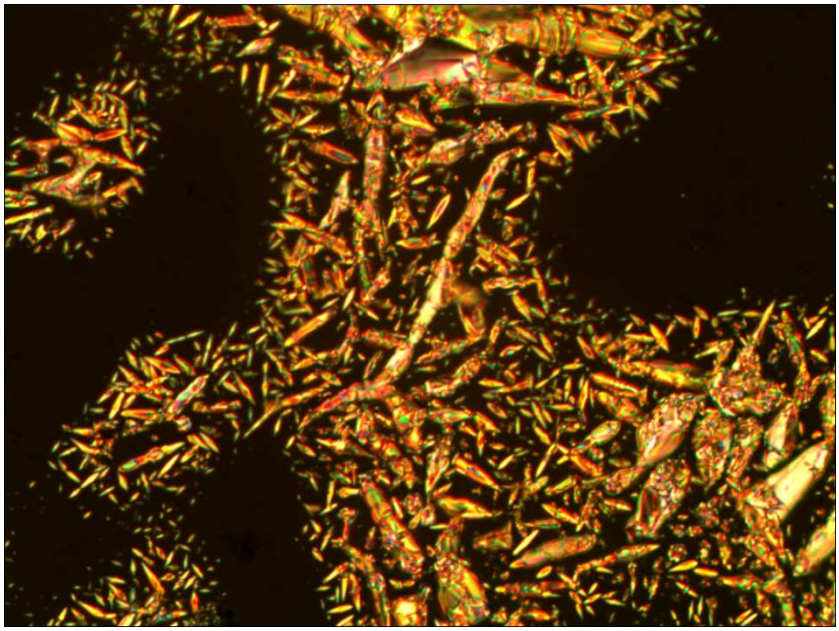


Figure 4: Photomicrograph showing the battonets with chiral line for ligands **7d** that coalesce to form the SmC* phase at 155.9 ^{o}C upon cooling.

DSC and polarizing microscope revealed that all the Cu(II) complexes exhibit enantiotropic chiral smectic A (SmA*) and SmC* phases. This finding indicates that the Cu(II) ion could suppress the formation of N* phase in complex **8a** as compared to the corresponding ligand **7a**. A noteworthy feature is that all the Cu(II) complexes show SmA* phase which is not observed in their uncoordinated ligands. The homogeneously aligned SmA* phase is evidenced by the presence of battonets that coalesce to form the well-defined focal conic fan-shaped texture (Figure 5). In addition, a pseudo-isotropic region typical of the SmA* phase is also observed. Further lowering of temperature from the SmA* phase led to the emerging of SmC* phase with chiral line (Figure 6). However, all the DSC thermograms for Cu(II) complexes do not show endothermic and exothermic peaks attributable to the SmA*-SmC* transition as the energy thus involved in this process is found to be too weak which is beyond the detection limit by DSC.

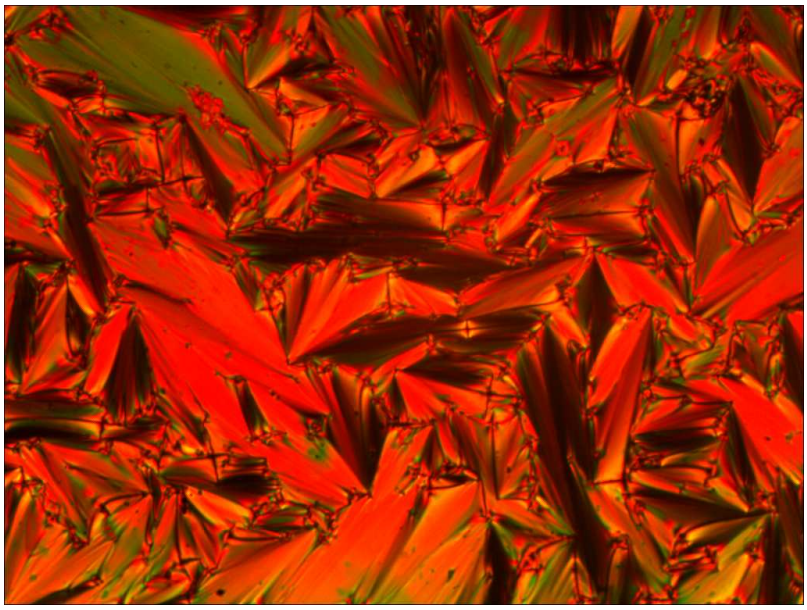


Figure 5: Photomicrograph showing the homogeneously aligned focal conic fan-shaped texture of SmA* phase for Cu(II) complex **8d** at 171.0 ^{o}C upon cooling.

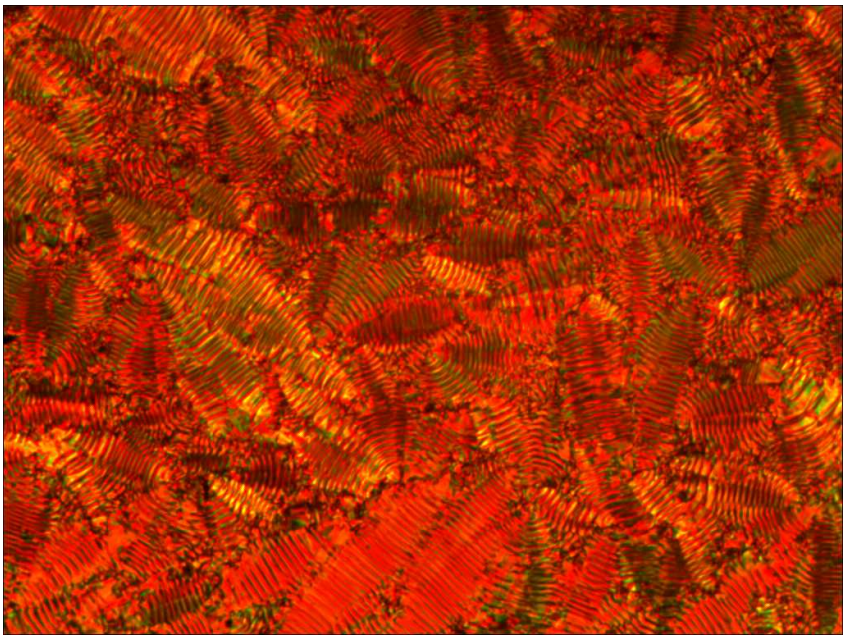


Figure 6: Photomicrograph showing the focal-conic fan texture of SmC* phase with chiral line in Cu(II) complexes **8d** at 140.2 ^{o}C upon cooling.

The induction of new SmA* phase in all complexes as compared to their uncoordinated ligands could be due to several reasons. This phenomenon can be ascribed to the difference in molecular geometry between the ligands and the Cu(II) complexes [34, 35]. Besides, the greater polarity of the coordination bonds and the increase of aromatic rings in the complexes enhance the lateral interactions between the molecules and consequently increase the smectogenicity of the complex [34, 35]. On the other hand, the [1,2,3]-triazole ring is commonly known to bring about the bending of the core system within the ligands and consequently deviation from linearity [11]. From the molecular modeling proposed by Srividhya and co-worker, the deviation angle is calculated as 33^{o} [11]. Upon complexation, the Cu(II) ion seems to increase the colinearity through the increase in aspect ratio of aromatic core to terminal flexible chain [3, 21-23, 27, 36-38]. This in turn could enhance the anisotropic properties and lateral interaction between the molecules and result in a new SmA* phase which is not observed in the ligands [3, 21-23, 27, 36-38]. The difference in term of the mesophase between the ligands and complexes also indicates a different molecular architecture could be achieved through the complexation [24].

The entropy changes, $\Delta S/R$ associated with the transition between N, SmC, SmA and I are listed in Tables 1 and 2. The ΔS values were obtained from $\Delta H/T$ in which T is the corresponding phase transition temperature in unit Kelvin, K and R is 8.314 $JK^{-1}mol^{-1}$. As

inferred from Tables 1 and 2, the $\Delta S_{SmC,I}/R$ for ligands are relatively higher than $\Delta S_{SmA,I}/R$ for complexes. This observation can further support the formation of new SmA phase in complexes, where the conversion of I to a less ordered SmA as compared to SmC phase will result in lower entropy value.

According to the transition temperature depicted in Figure 7, Table 1 and 2, all the Cu(II) complexes have relatively higher phase transition temperature as compared to their uncoordinated ligands. Upon complexation, the clearing temperatures increased by 30.6-39.4 ^{o}C indicating that all the Cu(II) complexes are thermally more stable than their uncoordinated ligands. This observation can be explained by the increase in molecular weight and the number of interacting sites upon formation of Cu(II) complexes.

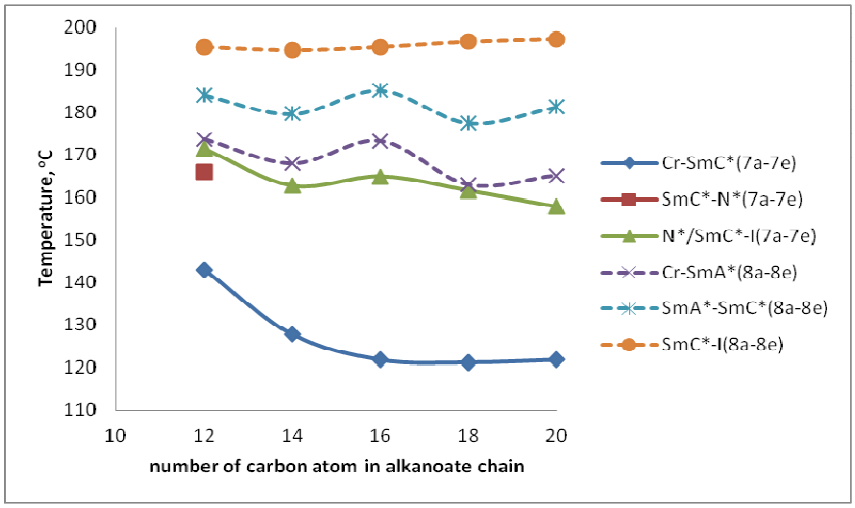
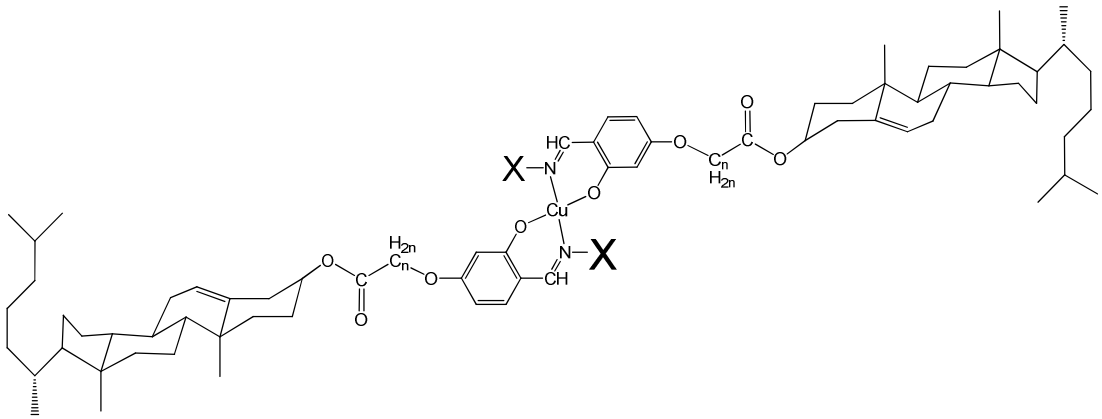
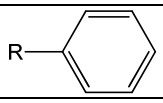
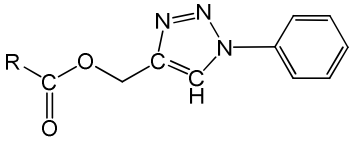


Figure 7: A plot of phase transition temperature upon heating versus the number of carbon atoms in alkyl chain for the ligands **7a–7e**, L (solid line) and their Cu(II) complexes **8a-8e**, CuL2 (dotted line).

3.2 Chemical structure–thermal and mesomorphic properties relationship

In order to rationalize the importance of different core systems resulted from the mesormorphic and thermal properties of Cu(II) complexes, the present homologous series of [1,2,3]-triazole, cholesterol-based dimesogenic Schiff bases ligands **7** and their corresponding Cu(II) complexes **8** are compared to the structurally related Cu(II) complexes synthesized by two different groups of researchers. The general molecular structure synthesized by these two research groups are shown below. Complexes **A** were synthesized by Shanker and co-worker [32], whereas complex **B** was obtained by Yelamaggad and co-worker [1]. Only complexes **8a** and **8c** from this study are chosen to compare with complexes **A** and **B** in order to ensure that the comparison is relevant.



Complex	X	Molecular weight	Terminal Chain, R (C_nH_{2n+1})	Spacer, C_nH_{2n}
A	R (Terminal chain)	1694.11	$C_{12}H_{25}$	C_7H_{14}
		1806.32	$C_{16}H_{33}$	
B		1734.09	$C_{10}H_{21}$	C_5H_{10}
8a and **8c**		2152.58	$C_{12}C_{25}$	C_7H_{14}
		2264.79	$C_{16}H_{33}$	

The ligand **7a** reported in this paper shows enantiotropic SmC* and N* phases whilst **7c** shows enantiotropic SmC* phase. However, the ligands in complexes **A** exhibit monotropic SmC* phase and enantiotropic SmA*, TGB and N* phases. On the other hands, ligand in complex **B** shows enantiotropic SmC*, SmA*, TGB and N*. A comparison between the present ligands **7a** and **7c** with earlier reported analogues reveal that the polymorphism in ligands **7** is suppressed. This can presumably be attributed to the non-colinearity of triazole ring which may

hinder the anisotropic behaviour [11]. Nevertheless, it is apparent that the SmC* phase induced by ligands **7a** and **7c** is more stable (enantiotropic) with larger mesomorphic range as compared to ligands in complexes **A** which exhibit monotropic SmC* phase. Apart from this, the thermal properties studies also reveal that the the ligands **7a** (171.3 ^{o}C) and **7c** (164.9 ^{o}C) with an additional aromatic and triazole ring are thermally more stable than the ligands (98.4 ^{o}C and 94.3 ^{o}C) in complexes **A**.

The earlier study on the analogous complexes **A** and **B** by Shanker and Yelamaggad had also shown explicit formation of monotropic SmA* phase and enantiotropic N* phase, respectively. This observation had led to conclude that Cu(II) ion acted against the presence of polymorphism. However, this phenomenon is found to be in contrary to our present finding. It is interesting to note that the Cu(II) complexes (**8a**, **8c** and other homologous compounds) reported in this paper generate a new SmA* phase which is not observed in their respective ligands. This finding further supports the explanation in section 3.1 in which the formation of complexes **8** is seemed to enhance the colinearity and thus increase the lateral interaction of non-linear ligands **7**.

It is worth to mention that SmC* phase is observed in the ligands **7** and Cu(II) complexes **8** prepared in this studies. The arrangement of molecules in enantiotropic SmA* and SmC* generated by Cu(II) complexes **8** is found to be more stable and ordered in comparison to monotropic SmA and N* phases observed in complexes **A** and **B**, respectively. These two observations indicate that the enhancement of SmA* and SmC* phases in ligands **7** and complexes **8** can be ascribed to the three nitrogen atoms from the triazole ring. The smaller atomic radius and higher electronegativity values of N atom as compared to C atom result in an elevated charged density in N atom [11]. The presence of high charge density heteroatom along with the polarity of carboxyl group from alkanoate chain could increase the polarizability of the molecule and thus enhance the dipole moment in the entire molecule [7, 11, 29]. This in turn will increase the dipole-dipole interaction and dielectric anisotropy between the molecules [7]. This type of intermolecular interaction and enhancement is essential for the induction of more ordered and stable lamellar packing. On the other hands, N atoms from triazole ring could create the force for tilting the resistance to tilt which can be achieved through the dipole-induce dipole and dipole-dipole interaction between the molecules [7, 29]. The reinforcement of this acentral transverse dipole led to the increasing in quadrupolar moment which would lead to the stabilization of SmC* phase [29].

A comparison in term of the thermal behaviors show that the clearing temperatures in complexes **8a** (192.3 ^{o}C) and **8c** (190.6 ^{o}C) are relatively higher than complexes **A** (160.0 ^{o}C, 120.2 ^{o}C) [39]. This could be rationalized by the presence of alkanoate-chain-triazole and aromatic rings in complexes **8a** and **8c** which increase the rigidity and intermolecular interaction.

4. Conclusion

A series of Cu(II) complexes containing 4,4'-disubstituted salicyldeneimine armed with two mesogenic units of [1,2,3]-triazole and cholesterol have been successfully synthesized. All the complexes and their uncoordinated ligands were elucidated by elemental analysis and spectroscopic techniques (UV-visible, FT-IR, ^{1}H-NMR). The lower homologous ligand, $C_{12}H_{25}$ shows enantiotropic N* and SmC* phase, whereas the other members with terminal alkanoate chain ranging from $C_{14}H_{29}$ to $C_{20}H_{41}$ exhibit SmC* phase. On the other hands, their corresponding Cu(II) complexes show enantiotropic SmA* and SmC* phases. A remarkable finding for this study is the induction of new SmA* phase in Cu(II) complexes which was absent in their ligands. Besides, the present study has disclosed that Cu(II) ion could increase the colinearity and the [1,2,3]-triazole ring could help in the stabilization of smectic phase.

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