Alkyl chain self ordering, induction and suppression of mesophase by Cu(II) containing [1,2,3]-triazole-based bidentate salicylaldimine ligands: synthesis, characterisation and X-ray diffraction studies

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Some new Cu(II) complexes containing [1,2,3]-triazole-based bidentate salicylaldimine and its analogues with terminal substituent (F, Cl, Br and I) have been synthesized. All the target complexes and their uncoordinated ligands were elucidated by elemental analysis and spectroscopic techniques (UV-visible, FT-IR, 1D, 2D 1H and 13C-NMR). The polarising optical microscope and differential scanning calorimetry (DSC) have disclosed all complexes and ligands are mesomorphic except the complex without any terminal substituent. The fluoro-substituted complexes with even parity C14H29 and C16H13 exhibit new enantiotropic nematic phase which was absent in their corresponding ligands, whereas the suppression of SmC phase occurred for all complexes with longer C14H13 and C16H17. X-ray diffraction confirmed the existence of SmA, SmC and N phases for complexes and ligands. The other notable feature is that the self-ordering of terminal alkyl chain occurred in SmA and SmC phases of complexes with even terminal alkyl chain ranging from C14H29 to C16H13. Their corresponding ligands exhibit intercalated structure of SmA and SmC phases. The thermal behaviour studies show that the fluoro-substituted triazole-based complexes possess lowest phase transition temperature and more stable as compared to other substituent which decomposed during the isotropisation.

Keywords: Cu(II) complexes; smectic C; triazole; salicylaldimine

1. Introduction

The interest towards metallomesogens and the recognition of their potential in technological development relating to advanced materials has shown a steady increase since last decade.[1] Various new molecule architectures which are difficult to achieve in conventional organic liquid crystal materials can be easily found in metal-containing liquid crystal, such as square planar, folder square, lantern, pyramidal and octahedral geometrical shapes.[2,3] In addition, the ionic metallomesogens led to better conductivity, charge transport and luminescence properties compared to conventional liquid crystalline systems.[4] From the chemical and physical viewpoints, the central metal ion can also enhance the ferroelectric properties and one-dimensional electrical conductivity apart from possessing variable oxidation state, colour and magnetism.[5–8] On the other hand, the metal ion is also capable to convert the non-mesogenic ligand to its metal-ligand complex possessing liquid crystalline properties.[9] This phenomenon can be attributed to the metal ions which enhance the anisotropic properties of non-mesogenic ligands.[10–14]

The most common design of liquid crystal is to confine the molecular core and the flexible chains of the molecule near the plane which display a high aspect ratio.[15] Metallomesogenic molecules containing transition metals can increase the ratio of aromatic core to terminal flexible chain leading to the enhancement of thermal stability of both crystalline and liquid crystal phases.[15,16] Moreover, metallomesogens also combine the unique properties of liquid-crystalline anisotropic fluids with the electronic and optical properties of metal complexes.[17]

Cu(II) metallomesogens with unpaired electron has been investigated extensively in the last two decades. The Cu(II) metallomesogens show interesting chemical and physical properties and offer a variety of potential application owing to the paramagnetism induced by Cu(II) centre.[9,18,19] It is well accepted that the metallomesogens containing unpaired electrons are paramagnetic liquid crystals, and the magnetic field strength thus required to align paramagnetic liquid crystals is much smaller than that required to align diamagnetic liquid crystals.[9,19–21] In 1989 and 1991, the mesomorphic as
well as paramagnetic properties of Cu(II) complexes had been studied extensively by Levelut and Ghedini together with their co-workers using PXRD and EPR techniques.[20,21] The latter had revealed that the introduction of paramagnetic ions in liquid crystalline materials can enhance the application of one-dimensional magnet in order to (i) repair defects in their structure,[22] (ii) obtain a magneto-optic data storage device,[19] and (iii) offer important routes to anisotropy materials that can be readily aligned in the devices.[23] The defects in a one dimension structure can be repaired by annealing a liquid crystalline material in the fluid phase, followed by quenching, thereby achieving relatively large-scale domain.[22]

Metal complexes derived from salicylaldimines are among the earliest and most widely studied classes of metallomesogens.[8,24] The salicylaldimine fragment is well recognised as a superb liquid crystalline material because the azomethine linkage can be easily formed and stabilised by intramolecular hydrogen bonding. As such, it has the ability to coordinate with metals.[8,9] Furthermore, it has been reported in recent years that liquid crystalline compounds with terminal 1,2,3-triazole ring induced the formation of smectic and nematic phases at low temperatures and/or over a wide temperature range.[25] Hence, different methods have been developed for the synthesis of 1,2,3-triazole ring, such as intramolecular cyclisation of bishydrazones or diazo intermediates, miscellaneous oxidations and three-component coupling (TCC).[26] But, the most common and successful method is the copper catalysed [3 + 2] dipolar cycloadition reaction between an organic azide and a terminal alkyne, which is also known as ‘click reaction’.[25,27,28]

It was claimed that the incorporation of this 1,2,3-triazole ring can result in remarkable changes in terms of liquid-crystalline phases and physical properties of the observed phases.[28,29] The change can be attributed to the endocyclic nitrogen atoms which are more polarisable than carbon.[25–28] Furthermore, the heterocyclic five-membered ring has the ability to increase molecular dipoles and dielectric anisotropy along with the changes in molecular shape.[23,26,29]

In this research, we introduce the 1,2,3-triazole-based bidentate salicylaldimine ligands in generating metallomesogens. The lack of any earlier report on Cu(II) metallomesogen with 1,2,3-triazole-based bidentate salicylaldimine and its substituted analogues possessing different terminal substituent (F, Cl, Br and I) has also prompted us to carry out the present study.

2. Experimental

2.1 Chemicals and reagents

4-hydroxybenzoic acid and sodium ascorbate were purchased from Sigma Aldrich. 2,4-dihydroxybenzaldehyde and propargyl bromide were purchased from TCI (Tokyo Chemical Industry). Similarly, 4-fluoronic, 4-chloroaniline, 4-bromoaniline and 4-iodoaniline were also obtained from TCI (Tokyo Chemical Industry). Copper(II) sulphate pentahydrate, copper (II) acetate dihydrate, potassium hydroxide and sodium azide were obtained from Qrec-Chemicals. 1-Bromodecane, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane and 1-bomoctadecane were purchased from Merck. All the chemicals as well as solvents were purchased commercially and used directly from the bottles without further purification.

2.2 Physical measurement

Structure of intermediary and title compounds were elucidated by Brucker Advance 300 MHz and 500 MHz ultrashield spectrometers equipped with ultrashield magnets. Deuterated chloroform (CDCl₃) and dimethylsulphoxide (DMSO-d₆) were used as solvents and TMS as internal standard. The IR spectra were recorded and measured on Perkin Elmer 2000-FTIR spectrophotometer in the frequency range 4000–400 cm⁻¹ with sample prepared in KBr discs. Thin layer chromatography was performed with TLC sheets coated with silica and spots were detected by UV irradiation. The elemental (C, H and N) analyses were carried out using a Perkin Elmer 2400 LS Series CHNS/O analyser. UV-visible spectra were recorded on a Perkin Elmer, Lambda 25 UV/Vis spectrometer. The ¹H and ¹³C NMR assignment of the title compounds were obtained and substantiated by 2D spectroscopic measurement such as ¹H-¹H correlation spectroscopy (COSY), ¹H,¹³C heteronuclear multiple quantum correlation (HMQC) and ¹H,¹³C heteronuclear multiple bond correlation (HMBC).

The phase transition temperatures and enthalpy values were measured by using a Seiko DSC6200R calorimeter with the heating and cooling rate of ±5° C. The Carl Zeiss Axioskop 40 polarising microscope equipped with a Linkam LTS 350 hot stage and TMS94 temperature controller were used for temperature-dependent studies and texture observation. The samples studied by optical microscope were prepared in a thin film sandwiched between glass slide and cover. Synchrotron powder X-Ray Diffraction (XRD) measurements were carried out at beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The X-ray
wavelength used for this study was 1.32633 Å. Besides, the XRD data were collected using imaging plates (IP, of an area = 20 × 40 cm² and a pixel resolution of 100) curved. The imaging plate curve has a radius equivalent to the sample-to-image plate distance of 280 mm and the diffraction signals were accumulated for 3 min. A capillary tube was used to pack the powder samples and heated by a heat gun, where the temperature controller was programmed by a PC with a proportional-integral-derivative (PID) feedback system. The scattering angle θ was calibrated by a mixture of silver behenate and silicon.

2.3 Synthesis

The bidentate salicylaldimine ligands 4 and their corresponding Cu(II) complexes 5 were prepared through the synthetic route as described in Scheme 1. The terminal alkynes intermediate 1 was prepared by the alkylation of 4-hydroxybenzoic acid with propargyl

Scheme 1. Synthetic routes toward formation of 4a-4e and their corresponding Cu(II) complexes.
bromide and followed by the steglich esterification with 2,4-dihydroxybenzaldehyde to obtain the intermediate 2. The compound 2 then underwent Cu(I) catalysed ‘click reaction’ with 1-azidoalkane (C₆H₂n₊₁ N₃; n = 10, 12, 14, 16 and 18) to afford the [1,2,3]-triazole ring compound 3. The triazole derivative thus obtained was subjected to condensation with aniline or halogenated aniline to yield the target Schiff base ligands 4 with different terminal substituent (F, Cl, Br and I). Finally, the reaction between ligands 4 with Cu(II) acetate dihydrate leads to the formation of the desired Cu(II) complexes 5 as brown solids. The chemical structures of the targeted ligands and their corresponding complexes were elucidated by FT-IR, ¹H-NMR, UV-visible spectrometer and elemental analysis. The codes for ligands 4 and their corresponding Cu(II) complexes 5 with different terminal substituent (F, Cl, Br and I) were shown in Scheme 1.

2.3.1 Synthesis of compound 1

4-hydroxybenzoic acid (3 g, 22 mmol) was dissolved in potassium hydroxide (2.4 g, 43 mmol) in 15 ml of water in a round bottom flask. The mixture was stirred until it dissolved and a solution of propargyl bromide (5.13 g, 43 mmol) in 10 mL ethanol was then added drop-wise. The resulting mixture solution was refluxed for 20 hours. 1.2 g of potassium hydroxide was subsequently dissolved in 5 ml of water and added into the mixture and continued to reflux for another 2 hours. After cooling, the resulting solution was neutralised with 10 ml diluted hydrochloric acid. The precipitate thus obtained was washed with distilled water and was recrystallised several times with ethyl acetate.

2.3.2 Synthesis of compound 2

An equivalent amount of compound 1 (1.6 g, 9 mmol) and dicyclohexylcarbodiimide, DCC were dissolved in dichloromethane (DCM) in a round bottom flask. 2,4-dihydroxybenzaldehyde (1.5 g, 10 mmol) was added to the mixture while stirring at room temperature followed by dimethyaminopyridine (0.2 g, 2 mmol), DMAP which was dissolved in sufficient amount of DCM. The reaction was stirred overnight. The precipitate was collected by filtration and recrystallised twice with chloroform.

2.3.3 Synthesis of 1-Azidoalkane

A round bottom flask containing 6 g of 1-bromoalkane and 2 equimolar of sodium azide in dimethylformamide, DMF was heated overnight at 70°C. The reaction mixture was then filtered and the filtrate was extracted twice with 50 ml DCM. The extract solution was evaporated at room temperature to give the yellow liquid product.

2.3.4 Synthesis of 1,2,3-triazole ring compound 3

A mixture containing compound 2 (100 mmol) and 1-azidoalkane (100 mol) in DMF was treated with 20-mole% of CuSO₄·5H₂O in DMF. While stirring, 20-mole% sodium ascorbate in minimum amount of water was added. The resulting mixture was stirred at room temperature for 24 hours. Water was then added and suction filtration was carried out on the mixture. The isolated yellow precipitate thus obtained was recrystallised several times with ethanol.

2.3.5 Synthesis of 1,2,3-triazole-based bidentate salicylaldimine ligands 4

In a round-bottom flask containing an equimolar of compound 3 with aniline or halogenated aniline in 30 mL absolute ethanol, few drops of catalytic amount of acetic acid were added. The resulting mixture was refluxed for 6 hours under continuous stirring. The precipitate thus obtained was recrystallised with ethanol to yield the desired ligands 4. Details on the percentage yield and analytical data for ligand 4 are available in electronic supporting material.

2.3.6 Synthesis of copper(II) complexes 5

In a round bottom flask, ligands 4 (2.0 mmol) was refluxed in a solvent mixture of ethanol and chloroform. An ethanolic solution of copper(II) acetate dihydrate (1.0 mmol) was then added drop-wise. The mixture solution was refluxed for 6 hours and then cooled to room temperature. The dark brown precipitate was collected by filtration, washed with hot ethanol and recrystallised twice by using chloroform-ethanol (1:1) to afford the desired Cu(II) complexes.

The percentage yields and analytical data for complexes 5 are summarised as below:

5aF: brown, yield 82%. Elemental analysis (IR (KBr) v_max/cm⁻¹: 1256 (C-O ether), 1267 (C-O phenolic), 1607 (C=C), 1614 (C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl)).

5bF: brown, yield 85%. Elemental analysis (IR (KBr) v_max/cm⁻¹: 1256 (C-O ether), 1267 (C-O phenolic), 1608 (C=C), 1614 (C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl)).

The percentage yields and analytical data for complexes 5 are summarised as below:

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5bF: brown, yield 85%. Elemental analysis (IR (KBr) v_max/cm⁻¹: 1256 (C-O ether), 1267 (C-O phenolic), 1608 (C=C), 1614 (C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl)).
5cF: brown, yield 81%. Elemental analysis (%): Found C 67.49, H 6.75, N 8.51; calculated (C_{74}H_{84}CuF_{2}N_{2}O_{3}), C 67.38, H 6.72, N 8.49%. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1255 (C-O ether), 1267 (C-O phenolic), 1608 (C=C), 1613 (C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl).

5dF: brown, yield 81%. Elemental analysis (%): Found C 68.31, H 7.08, N 8.16; calculated (C_{78}H_{90}CuF_{2}N_{2}O_{3}), C 68.12, H 7.04, N 8.15%. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1255 (C-O ether), 1267 (C-O phenolic), 1608 (C=C), 1614 (C=N), 1732 (C=O ester), 2918–2850 (C-H alkyl).

5eF: brown, yield 79%. Elemental analysis (%): Found C 68.90, H 7.34, N 7.80; calculated (C_{82}H_{90}CuF_{2}N_{2}O_{3}), C 68.81, H 7.32, N 7.83%. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1254 (C-O ether), 1266 (C-O phenolic), 1607 (C=C), 1614 (C=N), 1732 (C=O ester), 2918–2849 (C-H alkyl).

5aF: brown, yield 86%. Elemental analysis (%): Found C 63.20, H 5.92, N 9.09; calculated (C_{59}H_{50}Cl_{2}CuN_{2}O_{3}), C 63.94, H 5.85, N 9.04. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1251 (C-O ether), 1308 (C-O phenolic), 1605 (C=C and C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl).

5bF: brown, yield 84%. Elemental analysis (%): Found C 65.16, H 6.28, N 8.61; calculated (C_{70}H_{80}Cl_{2}CuN_{2}O_{3}), C 64.88, H 6.22, N 8.65. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1251 (C-O ether), 1307 (C-O phenolic), 1605 (C=C and C=N), 1734 (C=O ester), 2918–2849 (C-H alkyl).

5cF: brown, yield 78%. Elemental analysis (%): Found C 66.07, H 6.50, N 8.33; calculated (C_{71}H_{84}ClCuN_{2}O_{3}), C 65.74, H 6.56, N 8.29. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1251 (C-O ether), 1308 (C-O phenolic), 1606 (C=C and C=N), 1734 (C=O ester), 2918–2850 (C-H alkyl).

5dCl: brown, yield 88%. Elemental analysis (%): Found C 66.67, H 6.88, N 7.98; calculated (C_{78}H_{90}Cl_{2}CuN_{2}O_{3}), C 66.53, H 6.87, N 7.96. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1250 (C-O ether), 1308 (C-O phenolic), 1605 (C=C and C=N), 1733 (C=O ester), 2918–2850 (C-H alkyl).

5eCl: brown, yield 86%. Elemental analysis (%): Found C 67.57, H 7.14, N 7.67; calculated (C_{72}H_{84}Cl_{2}CuN_{2}O_{3}), C 67.26, H 7.16, N 7.65. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1250 (C-O ether), 1308 (C-O phenolic), 1605 (C=C and C=N), 1734 (C=O ester), 2918–2850 (C-H alkyl).

5dBr: brown, yield 76%. Elemental analysis (%): Found C 62.89, H 6.45, N 7.50; calculated (C_{78}H_{96}Br_{2}CuN_{2}O_{3}), C 62.58, H 6.46, N 7.49. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1252 (C-O ether), 1308 (C-O phenolic), 1605 (C=C and C=N), 1732 (C=O ester), 2920–2851 (C-H alkyl).

5dI: brown, yield 86%. Elemental analysis (%): Found C 59.05, H 6.02, N 7.01; calculated (C_{78}H_{96}CuI_{2}N_{2}O_{3}), C 58.88, H 6.08, N 7.04. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1252 (C-O ether), 1267 (C-O phenolic), 1605 (C=C and C=N), 1732 (C=O ester), 2920–2851 (C-H alkyl).

5dH: brown, yield 73%. Elemental analysis (%): Found C 70.28, H 7.36, N 8.39; calculated (C_{78}H_{96}CuI_{2}N_{2}O_{3}), C 69.95, H 7.38, N 8.37. IR (KBr) \( \nu_{\text{max}}/\text{cm}^{-1} \): 1253 (C-O ether), 1267 (C-O phenolic), 1605 (C=C), 1613 (C=N), 1733 (C=O ester), 2922–2851 (C-H alkyl).

3. Results and discussion

The detailed characterisation for FT-IR and UV-visible spectra for Cu(II) complexes 5 and their corresponding ligands 4 are available in electronic supporting information.

3.1 Thermal behaviour and liquid crystal properties

3.1.1 Liquid crystal properties

The phase transition temperature and associated enthalpies (kJ mol\(^{-1}\)) obtained from differential scanning calorimetry (DSC) are tabulated in Tables 1, 2, 3 and 4, respectively. DSC and polarising microscope revealed that the triazole-based ligand and its analogues with terminal fluoro, chloro, bromo and iodo substituents are enantiotropic. On the other hand, their corresponding Cu(II) complexes 5aF-5eF, 5aCl-5eCl, 5dBr and 5dI are also enantiotropic except the complex 5dH. When ligands 4aF, 4bF, 4aCl and 4bCl are cooled down from isotropic liquid, the nematic droplets appear and coalesce to form schlieren texture characteristics of N phase (Figure 1). Further cooling on 4aF, 4bF, 4aCl and 4bCl led to the formation of a well-defined focal conic fan-shaped texture of SmA phase followed by the broken fan-shaped texture of SmC phase as illustrated in Figures 2 and 3, respectively. The lengthening of terminal flexible chain from n = 14 to n = 18 in 4cF-4eF and 4cCl-4eCl has suppressed the presence of N phase. These ligands only exhibit enantiotropic SmA and SmC phases. This observation can be ascribed to the attraction between the long flexible terminal chains leading to their intertwining which facilitates the lamellar packing and is essential for the smectic phase.[30] The 4dBr and 4dI with terminal bromo and iodo-substituents exhibit the SmA and SmC phases as observed in 4dF and 4dCl. It is noteworthy that 4dH shows exclusively broken fan-shape of SmC phase only.

Under the polarising microscope, Cu(II) complexes 5aF-5eF are found to display enantiotropic N, SmA
Table 1. Phase transition temperatures (°C) and associated enthalpies (kJ mol$^{-1}$) of ligands 4aF-4eF and 4aCl-4eCl.

| Ligands | Cr$_1$ | Cr$_2$ | SmC | SmA | N | I |
|---------|--------|--------|-----|-----|---|---|
| 4aF     | Heating | 127.6 (1.2) | 134.4 (18.5) | 144.0$^a$ | 161.0$^a$ | 171.6 (0.8) |
|         | Cooling | 115.8 (−1.4) |        | 141.6$^a$ | 159.4 (−0.5) | 168.6$^a$ |
| 4bF     | Heating | 125.9 (7.7) | 131.2 (20.9) | 153.2$^a$ | 164.5 (1.0) | 169.4 (1.1) |
|         | Cooling | 112.8 (−31.4) |        | 147.0$^a$ | 158.8 (0.8) | 167.5 (−0.9) |
| 4cF     | Heating | 128.5 (35.1) |        | 155.7$^a$ |        | 171.5 (7.4) |
|         | Cooling | 108.1 (−34.7) |        | 148.5$^a$ |        | 168.2 (−6.4) |
| 4dF     | Heating | 93.9 (6.8) | 125.0 (30.1) | 151.6$^a$ |        | 171.7 (8.5) |
|         | Cooling | 102.0 (35.7) |        | 145.0$^a$ |        | 167.5 (−5.9) |
| 4eF     | Heating | 111.1 (17.2) | 125.9 (41.2) | 164.3$^a$ |        | 171.0 (9.6) |
|         | Cooling | 100.0 (−29.7) |        | 154.0 (−4.0) |        | 167.9$^a$ |
| 4aCl    | Heating | 135.7 (1.8) | 148.1 (22.4) | 158.0$^a$ | 178.6 (0.4) | 193.3 (1.0) |
|         | Cooling | 122.5 (−19.0) |        | 144.9 (−0.9) | 173.7$^a$ | 195.1$^a$ |
| 4bCl    | Heating | 87.6 (0.4) | 141.7 (31.2) | 160.0$^a$ | 189.9 (1.5) | 194.0 (0.8) |
|         | Cooling | 92.1 (−1.7) | 119.5 (−23.5) | 154.3$^a$ | 176.9 (−0.8) | 190.7$^a$ |
| 4cCl    | Heating | 91.4 (1.6) | 135.4 (21.9) | 157.2$^a$ |        | 195.5 (7.8) |
|         | Cooling | 117.3 (−28.1) |        | 151.6$^a$ |        | 177.0 (−2.8) |
| 4dCl    | Heating | 129.4 (11.1) |        | 169.5$^a$ |        | 199.8 (9.5) |
|         | Cooling | 114.7 (−22.2) |        | 158.4$^a$ |        | 185.3 (−5.5) |
| 4eCl    | Heating | 102.8 (6.1) | 127.0 (34.4) | 171.1$^a$ |        | 198.8 (9.6) |
|         | Cooling | 75.3 (−5.1) | 112.0 (−36.9) | 162.5$^a$ |        | 190.3 (−8.0) |

Notes: Cr, crystal; N, nematic; Sm C, smectic C; Sm A, smectic A; I, isotropic.
$^a$Denotes transition temperature derived from polarising optical microscope equipped with hot stage.

Table 2. Phase transition temperatures (°C) and associated enthalpies (kJ mol$^{-1}$) of ligands 4dBr, 4dI and 4dH.

| Ligands | Cr$_1$ | Cr$_2$ | SmC | SmA | I |
|---------|--------|--------|-----|-----|---|
| 4dBr    | Heating | 110.0 (6.7) | 136.3 (37.1) | 158.0$^a$ | 202.2 (9.2) |
|         | Cooling | 118.1 (−35.9) |        | 147.4$^a$ | 189.6 (−1.2) |
| 4dI     | Heating | 130.1 (24.4) | 142.9 (31.7) | 205.9$^a$ | 218.0$^a$ |
|         | Cooling | 125.6 (−2.4) |        | 197.6$^a$ | 211.6$^a$ |
| 4dH     | Heating | 95.3 (7.8) | 134.3 (52.4) |        | 152.0$^b$ |
|         | Cooling | 116.6 (−10.0) |        |        | 151.2$^a$ |

Notes: Cr, crystal; Sm C, smectic C; Sm A, smectic A; I, isotropic.
$^a$Denotes transition temperature derived from polarising optical microscope equipped with hot stage.
$^b$Denotes transition temperature derived from unresolved peaks.

(Figure 2) and SmC (Figure 3) phases resemble those observed in their uncoordinated ligands. Moreover, the Cu(II) complex 5dF exhibits enantiotropic ligands and SmA phases while complex 5eF shows exclusively SmA phase only. The chloro, bromo and iodo-substituted Cu(II) complexes 5aCl-5eCl, 5dBr and 5dI are enantiotropic but the isotropisation of these complexes is accompanied by decomposition. This phenomenon is further confirmed by DSC, where there is no exothermic transition observed during the cooling cycle.

Table 3 shows the heating on complexes 5aCl-5eCl from their crystal phases leading to the formation of SmC phase which is followed by the SmA phase. Further heating results in a change from SmA to N phase.

As inferred from DSC (Tables 3 and 4) and polarising microscope, the complexes 5dCl, 5eCl, 5dBr and 5dI exhibit only SmA phase. Tables 1 and 3 imply that the new N phase which is not found in uncoordinated ligands appears in their complex 5cF-5dF and 5eCl. Generally, long terminal flexible chain will cause intertwining and suppress the formation of N phase as observed in ligands 4cF-4eF with even parity C$_{12}$H$_{29}$-C$_{18}$H$_{37}$.[30] The presence of N phase in complexes with identical and even carbon numbers C$_{14}$H$_{29}$ and C$_{16}$H$_{33}$ can be resulted from the increase in the aspect ratio of the aromatic core to terminal flexible chain which in turn avoids the intertwining of terminal flexible chain. In addition, the Cu(II) ion can also enhance the anisotropic properties of the ligands and this is essential for N phase formation.[16] On the other hand, the formation of Cu(II) complexes also caused the suppression of SmC phase in all complexes with terminal alkyl chains C$_{16}$H$_{33}$ and C$_{18}$H$_{37}$. This indicates that the long terminal alkyl chains in complexes reduce the stability of SmC phase.
Table 3. Phase transition temperatures (°C) and associated enthalpies (kJ mol⁻¹) of complexes 5aF-5eF and 5aCl-5eCl.

| Complexes | Cr₁ | Cr₂ | SmC | SmA | N  | I   |
|-----------|-----|-----|-----|-----|----|-----|
| 5aF       | Heating • | 124.8 (3.0) | • | 185.9 (60.7) | • | 197.9⁺ | • | 201.0⁺ | • | 211.1 (1.2) | • |
|           | Cooling • | 117.7 (−1.0) | • | 193.0⁺ | • | 198.0⁺ | • | 203.6 (1.1) | • | 202.0a | • |
| 5bF       | Heating • | 193.5 (73.4) | • | 196.6⁺ | • | 198.6a | • | 202.0a | • |
|           | Cooling • | 129.1 (−44.0) | • | 187.0a | • | 197.0a | • |
| 5cF       | Heating • | 191.0 (73.3) | • | 191.9⁺ | • | 196.4 (1.0) | • | 199.9 (1.4) | • |
|           | Cooling • | 131.4 (−61.6) | • | 176.7⁺ | • | 185.1 (−0.5) | • | 191.7 (−1.0) | • |
| 5dF       | Heating • | 108.4 (3.6) | 177.7 (54.9) | • | 197.0⁺ | • | 199.1 (5.8) | • |
|           | Cooling • | 121.8 (−6.0) | • | 188.9⁺ | • |
| 5eF       | Heating • | 176.2 (63.0) | • | 200.3 (8.7) | • |
|           | Cooling • | 120.7 (−6.5) | • | 194.3⁺ | • |
| 5aCl      | Heating • | 162.3 (5.1) | 177.4 (50.3) | • | 197.0⁺ | • | 212.6⁺ | • | 233.3⁺ | • |
|           | Cooling • | 105.5 (9.3) | 174.0 (70.8) | • | 204.0⁺ | • | 219.0⁺ | • | 229.0⁺ | • |
| 5bCl      | Heating • | 165.9 (51.2) | • | 202.0⁺ | • | 218.9⁺ | • | 226.8 (4.2) | • |
|           | Cooling • | 121.4 (9.2) | 159.6 (36.8) | • | 229.5⁺ | • |
| 5cCl      | Heating • | 127.0 (16.1) | • | 227.0 (6.5) | • |

Notes: Cr, crystal; N, nematic; Sm C, smectic C; Sm A, smectic A; I, isotropic.
⁺Denotes transition temperature derived from polarising optical microscope equipped with hot stage.
⁻Denotes transition temperature derived from unresolved peaks.

Table 4. Phase transition temperatures (°C) and associated enthalpies (kJ mol⁻¹) of ligands 5dBr, 5dI and 5dH.

| Ligands | Cr₁ | Cr₂ | SmC | SmA | I   |
|---------|-----|-----|-----|-----|-----|
| 5dBr    | Heating • | 131.0 (10.0) | • | 184.9 (30.0) | • | 234.0⁺ | • |
| 5dI     | Heating • | 131.4 (52.8) | • | 242.0⁺ | • |
| 5dH     | Heating • | 121.4 (9.2) | • | 173.6 (71.5) | • |
|         | Cooling • | 145.1 (−67) | • |

Notes: Cr, crystal; Sm C, smectic C; Sm A, smectic A; I, isotropic.
⁺Denotes transition temperature derived from polarising optical microscope equipped with hot stage.

Figure 1. (colour online) Photomicrograph showing schlieren texture of nematic phases with two-brush and four-brush defects of ligands 4aF.

Figure 2. (colour online) Photomicrograph showing focal conic fan-shaped texture of SmA phase of Cu(II) complexes 5cF.
The coordination mode of the Cu(II) complexes resembles to the crystal structure of bis[4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene]copper(II) that appeared in our earlier report, in which both series involved salicylidene fragment as binding site. Thus, it is believed that the Cu(II) ion reported in this paper also possesses square planar geometry. Moreover, the square planar geometry of Cu(II) complexes can increase the geometrical anisotropy of molecules and is much favourable for mesophase formation compared to the tetrahedral geometry.

Table 5 shows the dependence of the entropy change, $\Delta S$ associated with the nematic–isotropic transition, expressed as the dimensionless quantity $\Delta S_{N,I}/R$, on terminal alkyl chain, $n$ for the ligands 4aF–4bF and complexes 5aF–5dF. It can be noticed from Table 5 that the $\Delta S_{N,I}/R$ is gradually increased with the lengthening of the even terminal alkyl chain from $n = 10$ to 12 for ligands and $n = 12$ to 16 for complexes. The elongation of terminal alkyl chain can lead to the reduction in uniaxiality of ligands and biaxiality of complexes. This in turn could enhance the orientational order of the nematic phase and give rise to the increase in $\Delta S_{N,I}/R$ with $n$.[32–34]

### 3.1.2 Thermal behaviour

The correlation studies between the transition temperature of Cu(II) complexes and ligands are depicted in Tables 1 to 4. All the Cu(II) complexes have higher phase transition temperatures compared to their uncoordinated ligands indicating that the introduction of a Cu(II) ion increases the phase transition temperature of the corresponding ligands. Besides, the clearing temperatures for all the Cu(II) complexes increased by 21–39°C upon complexation. This observation can be rationalised by the fact that the molecular weights as well as the number of interacting sites of Cu(II) complexes are higher in comparison to the ligands.[2]

It is worthwhile to mention that the increase in clearing temperature for this series of Cu(II) complexes is much lower than our earlier reported azobenzene-cored Cu(II) complexes [30] which showed increment of 60–70°C. This observation can be due to the non-linearity of 1,2,3-triazole ring that helps to lower the transition temperatures for the complexes.[25]

The influence of polar terminal group which is non-substituted or contains fluoro, chloro, bromo and iodo-substituents on the clearing temperatures of complexes can be illustrated in Figure 4. The iodo-substituted complexes have the highest clearing temperature followed by chloro, bromo, fluoro and their non-substituted analogues. Besides, their corresponding ligands also show the similar trend of clearing temperature as shown in Figure 4 and this observation is similar to the earlier reported non-symmetric dimer with

![Figure 3](image-url) Photomicrograph showing focal conic broken fan-shaped texture of SmC phase of Cu(II) complexes 5cF.

![Figure 4](image-url) A plot of clearing temperatures versus the number of carbon atoms in alkyl chain for the different substituents of Cu(II) complexes.

Table 5. The nematic to isotropic transition temperatures, $T_{N,I}$ (K), associated enthalpies, $\Delta H_{N,I}$ (kJ mol$^{-1}$), and entropy ($\Delta S_{N,I}/R$) of ligands 4aF–4bF and Complexes 5aF–5dF.

| Compounds | $T_{N,I}$ (K) | $\Delta H_{N,I}$ (kJ mol$^{-1}$) | $\Delta H/T$ | $\Delta S_{N,I}/R$ |
|-----------|---------------|---------------------------------|--------------|------------------|
| 4aF ($n = 10$) | 444.6 | 0.8 | 1.80 | 0.21 |
| 4bF ($n = 12$) | 442.4 | 1.1 | 2.49 | 0.30 |
| 5aF ($n = 10$) | 484.1 | 1.2 | 2.48 | 0.29 |
| 5bF ($n = 12$) | 476.7 | 1.1 | 2.31 | 0.28 |
| 5cF ($n = 14$) | 472.9 | 1.4 | 2.96 | 0.36 |
| 5dF ($n = 16$) | 472.1 | 5.8 | 12.29 | 1.48 |

Note: N, nematic; I, Isotropic.
octamethylene spacer.[34] The difference can be attributed to the variation in atomic sizes. Among all the elements, fluorine (1.47 Å) and hydrogen (1.2 Å) have the smaller atomic size as compared to chlorine, bromine and iodine.[35] This could be the reason why fluoro- and non-substituted complexes possess low clearing temperatures. In addition, high clearing temperatures for chloro, bromo and iodo-substituted complexes led to the decomposition of these complexes during the first heating process. Ligand 4 with different terminal substituent exhibits similar trend of clearing temperature as their Cu(II).

3.2 X-ray diffraction (XRD) studies

The liquid crystalline properties for 4aF-4eF and their corresponding Cu(II) complexes 5aF-5eF were further investigated by temperature dependent XRD. The XRD patterns of ligands 4aF and 4bF exhibit similar characteristics. Hence, a representative of XRD pattern for ligand 4bF is shown in Figure 5, while the detailed XRD information is tabulated in Table 6.

The XRD pattern from Figure 5 shows that at 160°C, a weak and broad peak is observed at a wide angle of \(2\theta = 29.5\)^°. This indicates that the liquid like arrangement of molecules or the lateral distribution of molecules is random. Thus, this confirms the formation of N phase during the cooling process. Upon further cooling from this phase to 140°C, a similar pattern of XRD diffraction is obtained with a remarkable decrease in \(d\)-layer spacing to 2.00 nm. This phenomenon reveals the transition of SmA phase to tiled structure of SmC phase with the tilt angle of 57.9°. Figure 7 shows the molecular arrangement of 4bF for SmA and SmC phases.

![Figure 5](image1.png)

**Figure 5.** (colour online) The XRD pattern of ligand 4bF upon cooling form 160°C to 130°C.

![Figure 6](image2.png)

**Figure 6.** Molecular modelling of ligand 4bF.

![Figure 7](image3.png)

**Figure 7.** (colour online) The molecular packing of 4bF for (a) SmA phase at 150°C and (b) SmC phase at 140°C.

| Temperature (°C) | \(2\theta\) (°) | d-spacing (nm) | Molecular distance (nm) | Tilt angle (°) |
|------------------|----------------|-----------------|------------------------|----------------|
| 160              | –              | 29.5            | 0.26                   | N              |
| 155              | 3.31           | 2.29            | 30                     | 0.26 N–SmA     |
| 150              | 3.21           | 2.36            | 30.1                   | 0.25 SmA       |
| 140              | 3.79           | 2               | 30.5                   | 0.25 SmC 57.9  |
| 130              | 3.41           | 2.22            | 30.5                   | 0.25 SmC 70.2  |

Note: N, nematic; Sm C, smectic C; Sm A, smectic A; N–SmA, the N phase transform to the SmA phase.
Figure 8 and Table 7 show the XRD pattern and detailed information for ligand 4cF upon cooling from 160°C. These results indicate that the ligand 4cF shows exclusively smectic phase below the isotropic phase. The $d$-spacings of 4cF reduces from 2.54, 2.20 nm (at 150°C) to 2.29, 2.03 nm (at 140°C), which confirms the transformation of SmA to SmC phase with a tilt angle of 64.4°. Interestingly, two sharp peaks at a low angle in a small angle X-ray scattering curve is observed for both SmA and SmC phases. The two sharp peaks at low angle contributing to the two $d$-layer spacing reflect the presence of a bilayer structure. One of the $d$-layer spacing is generated by the rigid core while the larger $d$-layer spacing is generated by the soft core. Figure 9 illustrates the intercalated molecular structure of 4cF for the SmA and SmC phases. The presence of intercalated structure is resulted from the terminal alkyl chain that is too long causing the dispersion between the molecules. The dispersion of molecules is more obvious at 140°C. The ligands 4dF and 4cF with longer terminal alkyl chain have the similar XRD pattern (Figure 9) and intercalated structure (Figure 9) as illustrated by 4cF.

As cooling from 195°C, the XRD studies reveal that Cu(II) complex 5bF with square planar geometry has the similar XRD patterns as the corresponding ligand 4bF. The detailed XRD information in Table 8 confirms the formation of N phase. In addition, the reducing $d$-layer spacing from 3.18 nm to 3.08 nm also substantiates the transformation from SmA to SmC phase. Besides, it can also be noted that the $d$-layer spacing for SmA phase of Cu(II) complex 5bF (3.18 nm) is much larger than the corresponding ligand 4bF (2.36 nm) and well compatible with the theoretical molecular length ($d/l = 1$) obtained from MM2 molecular calculation (Figure 10). Figure 11 illustrates the packing of molecules for 5bF in SmA and SmC phases with their corresponding $d$-layer spacing.

The formation of new N phase in complexes 5cF and 5dF can further be proven by the presence of broad peak at wide angle XRD curve with lateral packing at 20 = 16.1° (Table 9) and 20 = 15.3° (Table 10), respectively. From Table 9, the reducing $d$-layer spacing confirms the formation of SmA and SmC phases with tilt angle of 60.8°. Besides, the $d$-layer spacing found for both SmA (5.57 nm) and

**Table 7. The $d$-spacing, tilt angle and molecular distance of ligand 4cF obtained from XRD.**

| Temperature(°C) | 2θ(°) | d-spacing(nm) | 2θ(°) | Molecular distance(nm) | Phase | Tilt angle(°) |
|----------------|-------|---------------|-------|------------------------|-------|--------------|
| 160            | 3.17  | 3.6           | 2.39  | 2.1                    | 29.5  | 0.26         | SmA –          |
| 150            | 2.98  | 3.45          | 2.54  | 2.2                    | 29.8  | 0.26         | SmA –          |
| 140            | 3.31  | 3.74          | 2.29  | 2.03                   | 30.3  | 0.25         | SmC 64.4       |
| 130            | 3.12  | 3.64          | 2.43  | 2.08                   | 30.3  | 0.25         | SmC 73.1       |
| 120            | 3.17  | 3.64          | 2.39  | 2.08                   | 30.3  | 0.25         | SmC 70.2       |

Note: Sm C, smectic C; Sm A, smectic A.
SmC (4.86 nm) phases are much larger than the theoretical molecular length (3.42 nm) as shown in Figure 12. This phenomenon can be resulted from the presence of long alkyl chain which causes the self-assembly or ordering of the hydrophobic terminal alkyl chain. Table 10 and XRD pattern of complex 5dF in Figure 13 not only confirm the induction of new N phase but also prove the suppression of SmC phase by Cu(II) metal ion. Interestingly, the \( d \)-layer spacing is not only larger than the theoretical molecular length but it increases from 5.02 nm to 5.92 nm on cooling from 200°C to 180°C. This phenomenon can be explained by the self-ordering of the long terminal alkyl chain during the cooling process and this observation is very obvious with the lowering of temperature to 180°C. The molecular modelling in Figure 14 shows the packing and self-ordering of alkyl chain for complex 5dF. On the other hands, complex 5eF also shows the similar behaviour as 5dF. From the obtained XRD result, the self-ordering of alkyl chain only occurs in

| Temperature (°C) | \( 2\theta \) (°) | \( \text{d-spacing} \) (nm) | Molecular distance(nm) | Phase | Tilt angle (°) |
|------------------|----------------|-----------------------------|-------------------------|-------|---------------|
| 195              | –              | 15.6                        | 0.49                    | N     | –             |
| 190              | 2.38           | 3.18                        | 15.6                    | SmA   | –             |
| 185              | 2.46           | 3.08                        | 15.6                    | SmC   | 75.6          |
| 180              | 2.46           | 3.08                        | 15.7                    | SmC   | 75.6          |

Note: N, nematic; Sm C, smectic C; Sm A, smectic A.

SmC (4.86 nm) phases are much larger than the theoretical molecular length (3.42 nm) as shown in Figure 12. This phenomenon can be resulted from the presence of long alkyl chain which causes the self-assembly or ordering of the hydrophobic terminal alkyl chain. Table 10 and XRD pattern of complex 5dF in Figure 13 not only confirm the induction of new N phase but also prove the suppression of SmC phase by Cu(II) metal ion. Interestingly, the \( d \)-layer spacing is not only larger than the theoretical molecular length but it increases from 5.02 nm to 5.92 nm on cooling from 200°C to 180°C. This phenomenon can be explained by the self-ordering of the long terminal alkyl chain during the cooling process and this observation is very obvious with the lowering of temperature to 180°C. The molecular modelling in Figure 14 shows the packing and self-ordering of alkyl chain for complex 5dF. On the other hands, complex 5eF also shows the similar behaviour as 5dF. From the obtained XRD result, the self-ordering of alkyl chain only occurs in

![Figure 10. Molecular modelling of complex 5bF.](image)

![Figure 11. (colour online) The molecular arrangement of complex 5bF for (a) SmA phase at 190°C and (b) SmC phase at 185°C.](image)
complexes with longer terminal alkyl chain (n = 14, 16 and 18).

4. Conclusion

The mesogenic Cu(II) complexes with [1,2,3]-triazole-based salicylaldimine and its halogen-substituted analogues were successfully synthesised and characterised. All ligands and related Cu(II) complexes with various alkyl groups of even parity (n = 10–18) are enantiotropic except the complex in which the ligand consists of non-halogenated group. The Cu (II) ion has caused the induction of new N phase and suppression of SmC phase as compared to their uncoordinated ligands. All the mesophases observed in ligands and their corresponding complexes are further confirmed by temperature-dependent X-ray diffraction. Intercalated structures of SmA and SmC phase for ligands and alkyl chain self-ordering of complexes are only observed in even members of alkyl chain ranging from n = 14 to n = 18. The clearing temperatures of Cu(II) complexes are significantly higher as compared to the uncoordinated ligands. Besides, the fluoro-substituted complexes

Table 9. The d-spacing, tilt angle and molecular distance of complex 5cF obtained from XRD.

| Temperature (°C) | 2θ (°) | d-spacing (nm) | Molecular distance (nm) | Phase | Tilt angle (°) |
|-----------------|--------|----------------|------------------------|-------|---------------|
| 190             | –      | –              | 16.1                   | N     | 0.47          |
| 180             | 1.36   | 5.57           | 16.1                   | SmA   | 0.47          |
| 175             | 1.56   | 4.86           | 16.1                   | SmC   | 60.8          |
| 170             | 1.56   | 4.86           | 16.2                   | SmC   | 60.8          |
| 165             | 1.56   | 4.86           | 16.2                   | SmC   | 60.8          |
| 160             | 1.56   | 4.86           | 16.3                   | SmC   | 60.8          |

Note: N, nematic; Sm C, smectic C; Sm A, smectic A.

Table 10. The d-spacing, tilt angle and molecular distance of complex 5dF obtained from XRD.

| Temperature (°C) | 2θ (°) | d-spacing (nm) | Molecular distance (nm) | Phase | Tilt angle (°) |
|-----------------|--------|----------------|------------------------|-------|---------------|
| 210             | –      | –              | 15.3                   | N     | 0.5           |
| 200             | 1.51   | 5.02           | 15.7                   | SmA   | 0.48          |
| 190             | 1.51   | 5.02           | 16                     | SmA   | 0.48          |
| 180             | 1.28   | 5.92           | 16.1                   | SmA   | 0.47          |

Note: N, nematic; Sm A, smectic A.

Figure 12. (colour online) The molecular arrangement of complex 5cF for (a) SmA phase at 180°C and (b) SmC phase at 175°C.

Figure 13. (colour online) The XRD pattern of complex 5dF upon cooling from 210°C to 180°C.

Figure 14. (colour online) The molecular arrangement of complex 5dF for SmA phase at (a) 190°C and (b) at 180°C.
are mesogenic and possess lowest phase transition temperature as compared to the complexes consist of chloro-, bromo- and iodo-substituents.

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