New heterocyclic metallomesogens: synthesis, mesomorphic and thermal behaviours of Cu(II) complexes with 1,2,3-triazole-based Schiff bases ligands

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Two series of new Cu(II) complexes derived from the reaction of copper acetate with the non-linear 1,2,3-triazole-based Schiff bases have successfully been synthesised. The structures of the ligands and its complexes were elucidated by elemental analysis, FT-IR, \(^1\)H-NMR and UV–visible spectroscopic techniques. The differential scanning calorimetry and polarizing optical microscopy supported the anisotropic properties of uncoordinated ligands in which the focal conic fan-shaped texture and/or broken fan-shaped texture characteristics of respective SmA and SmC phases were recorded. However, not all of their corresponding Cu(II) complexes are mesogenic. Although the iodo-substituted ligands with even parity C\(_{10}\)H\(_{25}\) to C\(_{14}\)H\(_{31}\) are non-stable and exhibit SmA phase which is not reproducible, the ultimate Cu(II) complexes show exclusively stable SmA phase. This observation can be ascribed to the enhanced colinearity and molecular anisotropic by the presence of Cu-N and Cu-O coordination modes. On the other hand, the comparison studies show that different positions of ortho-hydroxyl group affect the mesomorphic and thermal behaviour of ligands and Cu(II) complexes.

**Keywords:** Cu(II) complexes; SmA; SmC; triazole

1. Introduction

The design of novel mesomorphic compounds as advanced functional materials involves the selection of a core fragment, polar linking group as well as terminal substituent. One of the designs which had been selected since a decade ago was the heterocyclic five-membered ring, but this type of compound displayed non-linearity and less mesogenic stability.[1–3] Generally, the heterocyclic ring had been adopted as a core unit in thermotropic liquid crystals owing to its ability to impart lateral and longitudinal dipoles along with the changes in the molecular shape.[1,2,4,5] Furthermore, the incorporation of heteroatoms may result in the changes of physical properties particularly the liquid-crystalline phases as the nitrogen atoms in the ring are considered more polarisable than carbon.[1,4,5]

There are several reported methods relating to the synthesis of N-heterocyclic five-membered [1,2,3]-triazole ring.[1] However, the widely used and most successful method is the copper-catalysed [3 + 2] dipolar cycloaddition reaction which is also known as ‘click reaction’.[1,2,6–8] Apart from using copper as catalyst, this reaction also requires an organic azide and terminal alkyne as precursors. In order to give desired compounds with lower melting points and to generate a range of different liquid crystalline mesophases, Srividhya and co-worker had incorporated the [1,2,3]-triazole ring into the principal structure of calamitic mesomorphic materials.[2] This type of material possesses great potential in advance material chemistry and displays high biological activity.[1,9,10]

Another interesting field is based on the metal containing liquid crystal or metallomesogen. This complex is capable of exhibiting unique features which may not be possible in conventional organic liquid crystals, for instance, the formation of mesogenic complexes from non-mesogenic ligands.[11–15] Ferroelectric properties and one-dimensional electrical conductivity.[13,14,16,17] The resulting metal complexes are more suitably oriented for the fortification properties due to the high polarity of coordination bond.[14] Besides, the difference in geometrical shapes, richness in oxidation state, colour, magnetism possessed by metal ions and redox behaviour are the additional properties of metallomesogen.[18,19] On the other hand, the formation of complexes can also cause a dramatic effect on the thermal and liquid crystal behaviour of the uncoordinated ligands.[20]

In this paper, the 1,2,3-triazole system will be introduced in metallomesogens. Despite knowing

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that the high melting temperature of Cu(II)-metallo-
mesogens always leads to decomposition and hence
limit the application of these materials, the non-line-
arity of 1,2,3-triazole ring was claimed to be able to
overcome the shortcoming by lowering the melting
temperature and thus prevent the decomposition of
Cu(II)-metallomesogens. Besides, the scarcity of report
on liquid crystalline materials containing 1,2,3-triazole
system especially in metallomesogens has also
prompted us to carry out the present work aiming at
synthesizing the Cu(II) complexes and evaluating the
structure–property relationship in terms of thermal and
mesomorphic behaviour for these complexes and their
uncoordinated 1,2,3-triazole-based ligands.

2. Experimental

2.1 Materials and methods

4-Bromosalicylaldehyde, propargyl bromide and 2,4-
dihydroxybenzaldehyde were purchased from TCI
(Tokyo Chemical Industry, Tokyo, Japan) while
sodium bicarbonate was obtained from R&M-
Chemicals (Edmonton, AB, Canada). Copper(II)
sulphate pentahydrate was obtained from Qrec-
Chemicals (Penang, Malaysia), whereas 4-acetami-
dophenol and sodium ascorbate were purchased
from Sigma Aldrich (St. Louis, MO, USA). 1-
Bromodecane, 1-bromododecane, 1-bromotetradecane,
1-bromohexadecane and 1-bromooctadecane were sup-
pplied by Merck (Darmstadt, Germany). Besides, 4-
fluoroaniline and copper(II) acetate dihydrate were pur-chased from Acros-Chemical (Geel, Belgium). All
reagents were used without further purification.

The chemical structures of intermediates and tar-
get materials were analysed by Bruker Avance 300
and 500 MHz UltraShield spectrometers equipped
with UltraShield magnets. Deuterated chloroform
(CDCls) and dimethylsulphoxide (DMSO-d6) were
used as solvents and TMS as an internal standard.
The FT-IR spectra were recorded 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) analysis
was 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 phase transition temperatures and enthalpy
values were measured by a Seiko DSC6200R calorimeter
with the heating and cooling rates of ±5°C. The
liquid crystal textures of all compounds were ob-
served by Carl Zeiss Axioskop 40 polarizing micro-
scope equipped with a Linkam LTS 350 hot stage and
TMS94 temperature controller. The samples studied
by optical microscope were prepared in a thin film
sandwiched between glass slide and cover.

2.2 Synthesis (Scheme 1)

2.2.1 N-(4-(prop-2-ynyloxy)phenyl)acetamide

A mixture containing 5.0 g (33 mmol) of 4-acetam-
dophenol, 2 equimolar of sodium carbonate and cat-
alytic amount of potassium iodide in acetone was
placed in a round bottom flask with stirrer. Two
equimolar of propargyl bromide was added dropwise
into this solution. The resulting reaction was refluxed
overnight and then filtered to get rid of the sodium
carbonate and potassium iodine. The filtrate was eva-
porated to dryness, and the precipitate thus obtained
was washed with distilled water. The product was
purified with ethanol via recrystallisation.

2.2.2 Synthesis of 1-azidoalkane

1-Bromoalkane (6.0 g) and 2 equimolar of sodium
azide were dissolved in dimethylformamide (DMF)
and then heated overnight at 70°C. The reaction mix-
ture was then filtered, and the filtrate was extracted
twice with 50 ml dichloromethane. The extracted
solution was evaporated at room temperature to
give a pure yellow liquid product.

2.2.3 N-(4-((1-alkyl-1H-1,2,3-triazol-4-yl)methoxy)
phenyl)acetamide

A mixture of 1-azidoalkane and N-(4-(prop-2-yny-
loxy)phenyl)acetamide in DMF with 20-mole % Cu.
SO₄·5H₂O and 20-mole % sodium ascorbate was stir-
ered at room temperature for overnight. The mixture
was then poured into cold water, and the resulting
precipitate was filtered by Buchner funnel. The iso-
lated compound thus obtained was recrystallised sev-
eral times from ethanol.

2.2.4 4-(alkoxy)-2-hydroxybenzaldehyde

2,4-Dihydroxybenzaldehyde (3.0 g, 22 mmol), cataly-
tic amount of potassium iodide, 1 equivalent of
sodium carbonate and 1 equivalent of 1-alkanebromo
were mixed in dry acetone. The reaction mixture
was heated overnight. The reaction mixture was then fil-
tered to remove any insoluble solid, and the filtrate
was evaporated to dryness. The precipitate thus ob-
tained was washed with distilled water and purified
by column chromatography using a mixed solvent
system containing chloroform and hexane (V/V, 1/1)
as eluent. Evaporation of the solvents gave the pro-
duct a white solid.
Scheme 1. Synthetic routes towards formation of 1a16-1e16, 1aBr-1eBr and their corresponding Cu(II) complexes 2a16-2e16 and 2aBr-2eBr.
2.2.5 Synthesis of triazole-based bidentate Schiff bases 1

An ethanolic solution of 4-bromosalicylaldehyde or 4-(hexadecanoyloxy)-2-hydroxybenzaldehyde was added slowly into a hot ethanolic solution of N-(4-((1-alkyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)acetamide in a two-neck round bottom flask. The resulting mixture was refluxed for 6 hr under continuous stirring. The mixture was then concentrated by evaporating ethanol at room temperature and the precipitate thus obtained was recrystallised from ethanol to yield the desired product. The percentage yield and detailed analytical data (CHN, FT-IR and 1H-NMR) for a representative ligand 1a16 are shown below. The data for the remaining ligands are available in Supplemental data.

1a16: light yellow, yield 45%. Elemental analysis/\%: Found C 75.05, H 9.99, N 8.29; calculated (C_{26}H_{46}N_{2}O_{5}), C 74.73, H 9.87, N 8.30. IR (KBr) \nu_{\text{max}}/\text{cm}^{-1}: 1259 (C–O ether), 1290 (C–O phenolic), 1599 (C=C), 1627 (C=N), 2922 (C–O ether), 1283 (C–O phenolic), 1571 (C=C), 1625 (C=N), 2916 (C–O ether), 1315 (C–O phenolic), 1597 (C=C), 1616 (C=N), 2922–2851 (C–H alkyl).

2.2.6 Synthesis of Cu(II) complexes 2

Triazole-based bidentate Schiff bases (2 mmol) were refluxed in ethanol. An ethanolic solution of copper(II) acetate dihydrate (1 mmol) was then added dropwise to an ethanolic solution containing 4-((1-alkyl-1H-1,2,3-triazol-4-yl)methoxy)-2-hydroxybenzaldehyde. The resulting mixture was refluxed for 6 hr under continuous stirring. After cooling, the mixture was concentrated by evaporating ethanol at room temperature and the precipitate thus obtained was recrystallised from ethanol to yield the desired product. Following are the percentage yield and detailed analytical data (CHN and FT-IR) for a representative Cu(II) complex 2a16. The data for the remaining complexes are available in Supplemental data.

2a16: brown, yield 86%. Elemental analysis/\%: Found C 72.39, H 9.41, N 8.04; calculated (C_{68}H_{130}CuN_{2}O_{5}), C 72.30, H 9.39, N 8.03. IR (KBr) \nu_{\text{max}}/\text{cm}^{-1}: 1241 (C–O ether), 1315 (C–O phenolic), 1597 (C=C), 1616 (C=N), 2922–2851 (C–H alkyl).

2.3 Synthesis (Scheme 2)

2.3.1 Synthesis of 2-hydroxy-4-(prop-2-ynyloxy) benzaldehyde

In a round bottom flask containing 5.0 g (36 mmol) of 2,4-dihydroxybenzaldehyde, catalytic amount of potassium iodide, 1 equimolar of sodium bicarbonate in acetone and 1 equimolar of propargyl bromide were then added. The reaction mixture was left to reflux under continuous stirring for overnight. The mixture was then filtered and the filtrate was evaporated to dryness. The precipitate thus obtained was washed with distilled water and purified by column chromatography eluting with a mixture of chloroform and hexane (V/V, 1/1). Evaporation of the solvents gave the product as a white solid.

2.3.2 Synthesis of 1-azidoalkane

The preparation of 1-azidoalkane was carried out via the similar method described in section 2.1.1.

2.3.3 Synthesis of 4-((1-alkyl-1H-1,2,3-triazol-4-yl) methoxy)-2-hydroxybenzaldehyde

The synthesis of 1,2,3-triazole derivatives was carried out via the similar method described in 2.1.3 wherein the N-(4-prop-2-nyloxy)phenylacetamide was replaced by 2-hydroxy-4-prop-2-nyloxybenzaldehyde.

2.3.4 Synthesis of triazole-based bidentate Schiff bases 3

4-Chloroaniline, 4-bromoaniline or 4-iodoaniline (100 mmol) was dissolved in ethanol and then added dropwise to an ethanolic solution containing 4-((1-alkyl-1H-1,2,3-triazol-4-yl)methoxy)-2-hydroxybenzaldehyde. The resulting mixture was refluxed for 6 hr under continuous stirring. After cooling, the mixture was concentrated by evaporating ethanol at room temperature and the precipitate thus obtained was recrystallised from ethanol to yield the desired product. Following are the percentage yield and detailed analytical data (CHN, FT-IR and 1H-NMR) for a representative ligand 3aCl. The data for the remaining ligands are available in Supplemental data.

3aCl: yellow, yield 41%. Elemental analysis/\%: Found C 66.97, H 7.15, N 11.96; calculated (C_{26}H_{30}N_{2}O_{2}), C 66.58, H 7.09, N 11.95. IR (KBr) \nu_{\text{max}}/\text{cm}^{-1}: 1247 (C–O ether), 1283 (C–O phenolic), 1571 (C=C), 1625 (C=N), 2916–2848 (C–H alkyl), 3441 (O–H). 1H NMR (300 MHz, CDCl_{3}), \delta (ppm): 0.87 (t, 6H, CH_{3}), 1.34–1.94 (m, 16H, CH_{2}), 4.39 (t, 2H, OCH_{2}), 5.26 (s, 2H, OCH_{2}), 6.59–6.62 (m, 2H, Ar–H), 7.21 (d, 2H, Ar–H), 7.30 (d, 1H, Ar–H), 7.35 (d, 2H, Ar–H), 7.69 (s, 1H, N–CH), 8.52 (s, 1H, N=CH), 13.50 (s, 1H, Ar–OH).

2.3.5 Synthesis of Cu(II) complexes 4

The synthesis of Cu(II) complexes was carried out using the same method described in section 2.1.6.
Following are the percentage yield and detailed analytical data (CHN and FT-IR) for a representative Cu(II) complex 4aCl. The data for the remaining complexes are available in Supplemental data.

4aCl: brown, yield 89%. Elemental analysis/\%: Found C 62.59, H 6.44, N 11.22; calculated (C_{52}H_{64}CuN_{8}O_{4}) C 62.48, H 6.45, N 11.21. IR (KBr) \nu_{max}/\text{cm}^{-1}: 1250 (C=O ether), 1324 (C=O phenolic), 1589 (C=C), 1601 (C=N), 2917–2850 (C–H alkyl).

3. Result and discussion

3.1 Mesomorphic and thermal behaviour

3.1.1 Mesomorphic properties

The detailed synthesis, characterisation, FT-IR, UV–visible spectra for Cu(II) complexes 2, 4 and their corresponding ligands 1, 3 are available in electronic supporting information. The transition temperatures and associated enthalpies (kJ mol\(^{-1}\)) are shown in Tables 1–6. The ligands 1aI-1eI and 1aBr-1eBr are enantiotropic, whereas their corresponding

Scheme 2. Synthetic routes towards formation of 3aCl-3eCl, 3aBr-3eBr, 3aI-3eI and their corresponding Cu(II) complexes 4aCl-4eCl, 4aBr-4eBr and 4aI-4eI.
Table 1. Phase transition temperature (°C), associated enthalpies (kJ mol$^{-1}$) and entropy ($\Delta S$/R) of ligands 1a16-1e16 and 1aBr-1eBr.

| Ligand | Cr$_1$ | Cr$_2$ | SmC | SmA | I | $\Delta S_{SmC}$/R | $\Delta S_{SmA}$/R |
|--------|--------|--------|-----|-----|---|----------------|-----------------|
| 1a16   | Heating • | 122.9 (45.3) | • | 143.3 (11.2) | • | 3.2 |
|        | Cooling • | 117.8 (62.3) | • | 143.0 (16.2) | • | 4.6 |
| 1b16   | Heating • | 89.8 (8.6) | • | 121.6 (41.6) | • | 3.1 |
|        | Cooling • | 77.6 (20.3) | • | 109.7 (43.2) | • | 4.3 |
| 1c16   | Heating • | 101.1 (14.3) | • | 122.8 (48.7) | • | 3.0 |
|        | Cooling • | 131.6 (3.5) | • | 112.2 (44.0) | • | 4.5 |
| 1d16   | Heating • | 105.1 (9.2) | • | 124.4 (53.1) | • | 6.2 |
|        | Cooling • | 101.5 (21.5) | • | 113.4 (59.7) | • | 6.2 |
| 1e16   | Heating • | 115.5 (35.0) | 126.4 (71.9) | • | 140.3 (22.0) | • | 6.4 |
|        | Cooling • | 114.7 (113.3) | 140.4 (21.5) | • | 6.2 |
| 1aBr   | Heating • | 116.6 (7.4) | • | 138.2 (34.6) | • | 3.1 |
|        | Cooling • | 123.5 (34.8) | • | 141.3 (11.3) | • | 3.2 |
| 1bBr   | Heating • | 124.5 (3.1) | • | 131.5 (31.9) | • | 3.3 |
|        | Cooling • | 121.0 (32.8) | • | 146.7 (11.7) | • | 3.3 |
| 1cBr   | Heating • | 131.1 (55.9) | • | 151.3 (14.1) | • | 3.9 |
|        | Cooling • | 118.2 (9.3) | • | 149.7 (13.7) | • | 3.8 |
| 1dBr   | Heating • | 130.4 (56.5) | • | 152.2 (13.6) | • | 3.8 |
|        | Cooling • | 115.9 (47.7) | • | 150.6 (13.0) | • | 3.6 |
| 1eBr   | Heating • | 130.7 (66.1) | • | 152.5 (14.3) | • | 4.0 |
|        | Cooling • | 115.2 (54.1) | • | 151.0 (13.6) | • | 3.8 |

Note: Cr$_1$, crystal 1; Cr$_2$, crystal 2; SmC, Smectic C; SmA, Smectic A; I, isotropic.

Table 2. Phase transition temperature (°C), associated enthalpies (kJ mol$^{-1}$) and entropy ($\Delta S$/R) of complexes 2a16-2e16 and 2aBr-2eBr.

| Complex | Cr$_1$ | Cr$_2$ | I | $\Delta S$/R |
|---------|--------|--------|---|-------------|
| 2a16    | Heating • | 123.4 (35.4) | • | 181.9 (87.5) | • | 23.1 |
|        | Cooling • | 136.3 (19.7) | • | 171.8 (62.6) | • | 16.9 |
| 2b16    | Heating • | 118.3 (47.5) | • | 176.0 (75.3) | • | 20.1 |
|        | Cooling • | 105.5 (31.5) | • | 171.5 (61.5) | • | 16.6 |
| 2c16    | Heating • | 121.6 (45.5) | • | 178.3 (79.6) | • | 21.2 |
|        | Cooling • | 120.8 (27.9) | • | 173.7 (73.6) | • | 19.8 |
| 2d16    | Heating • | 119.1 (50.7) | • | 176.9 (81.8) | • | 21.8 |
|        | Cooling • | 81.3 (51.9) | • | 172.1 (80.0) | • | 21.6 |
| 2e16    | Heating • | 115.5 (59.6) | • | 172.0 (80.8) | • | 21.8 |
|        | Cooling • | 102.4 (34.8) | • | 171.7 (73.8) | • | 19.9 |
| 2aBr    | Heating • | 151.9 (2.9) | • | 183.6 (51.4) | • | 13.5 |
|        | Cooling • | 139.4 (11.3) | • | 147.3 (46.1) | • | 13.2 |
| 2bBr    | Heating • | 103.5 (15.1) | • | 180.9 (49.1) | • | 13.0 |
|        | Cooling • | 80.2 (3.0) | • | 172.5 (44.2) | • | 11.93 |
| 2cBr    | Heating • | 88.7 (4.8) | • | 181.8 (45.9) | • | 12.1 |
|        | Cooling • | 54.7 (8.3) | • | 133.6 (38.2) | • | 11.3 |
| 2dBr    | Heating • | 90.2 (28.4) | • | 180.9 (52.1) | • | 13.8 |
|        | Cooling • | 74.6 (13.4) | • | 139.4 (36.2) | • | 10.5 |
| 2eBr    | Heating • | 108.8 (21.3) | • | 180.6 (46.6) | • | 12.3 |
|        | Cooling • | 141.0 (38.6) | • | 32.8 |

Note: Cr$_1$, crystal 1; Cr$_2$, crystal 2; I, isotropic.

Cu(II) complexes are non-mesogenic. On cooling ligands 1a16-1e16 from the isotropic, batonnets developed and coalesced to form broken fan-shaped texture characteristics of SmC phase (Figure 1). On the other hand, ligands 1aBr-1eBr with terminal bromo-substituent exhibit enantiotropic SmA phase. The presence of SmA phase can be supported by the formation of batonnets that coalesce to form the focal conic fan-shaped texture (Figure 2). Optical observation shows that Cu(II) complexes 2a16-2e16 and 2aBr-2eBr have clearly melted and transformed into isotropic phase at 172.0–183.0°C. In addition, the differential scanning calorimetry curve for these two series of complexes exhibits only strong
endothermic (crystal to isotropic) and exothermic (isotropic to crystal) transitions. Apparently, this can be associated with the transition of well-organised crystal phase to isotropic phase. The ligands 1a16-1e16 with one terminal alkyl group and another terminal n-hexadecanoyloxy exhibit a tilted SmC phase as compared to SmA phase in ligands 1aBr-1eBr. This can be explained by the long n-hexadecanoyloxy in ligands 1a16-1e16 favouring the intermolecular interaction and intertwining, which in turn facilitate the lamellar packing, leading to the formation of tilted mesophase.[21]

The ligands 3 and their Cu(II) complexes 4 with terminal chloro-, bromo- and iodo-substituents show monotropic or enantiotropic SmA phase with typical focal conic fan-shaped textures. The ligands 3aCl-3eCl and 3aBr-3eBr exhibit exclusively enantiotropic SmA phase, which are reproducible upon heating and cooling. Surprisingly, their corresponding Cu(II) complexes 4 with shorter alkyl chain, n = 10,12 and 14, show monotropic SmA phase only. This could be due to the shorter alkyl chain that may not be able to maintain the aspect ratio to impart the enantiotropic mesophase. Further lengthening of the flexible alkyl chain to n = 16 and 18 induced the formation of enantiotropic SmA phase as shown in Figure 3.[22]

Optical observation supports that ligands 3aI-3cI with iodo-substituent show monotropic SmA phase that is not reproducible upon subsequent heating and cooling. The first cooling from isotropic liquid to SmA phase.
as experienced by the ligands with shorter flexible chain shows the existence of batonnets. However, the batonnets are suppressed by the formation of crystal phase and these two phases occur at the same time. On the other hand, the longer terminal alkyl chain ligands 3dI-3eI (n = 16 and 18) generate a stable monotropic SmA phase which are reproducible upon subsequent heating and cooling. This observation supports that the hydrophobic interaction between the longer terminal flexible chain can stabilise the SmA phase.[16]

On contrary to the non-stable SmA phase behaviour observed in ligands 3aI-3dI, their Cu(II) complexes 4aI-4dI display enantiotropic SmA phase as compared to monotropic SmA phase behaviour observed in their uncoordinated ligands 3dI-3eI. These findings indicate that the metal ion can stabilise the mesophase through the increase in the aspect ratio of aromatic core to terminal flexible chain.[23] Besides, the formation of Cu(II) complexes 4aI-4dI can also increase the colinearity and thus enhance the anisotropic properties of these non-linear ligands.[13,24] Figure 4 shows the summary of mesophase for ligands and their Cu(II) complexes.

Table 1–6 show the entropy changes associated with the transition between Cr, SmA, SmC and I of which the entropy change is expressed in the tables. The transition temperature (°C), associated enthalpies (kJ mol\(^{-1}\)) and entropy (\(\Delta S/R\)) of complexes 4aCl-4eCl and 4aBr-4eBr are summarised in Tables 5 and 6. 

**Table 5. Phase transition temperature (°C), associated enthalpies (kJ mol\(^{-1}\)) and entropy (\(\Delta S/R\)) of complexes 4aCl-4eCl and 4aBr-4eBr.**

| Complex     | Cr\(_1\) | Cr\(_2\) | SmA  | I   | \(\Delta S_{Cr,I}/R\) | \(\Delta S_{SmA,I}/R\) |
|-------------|----------|----------|------|-----|----------------------|-----------------------|
| 4aCl        | Heating  |          | 174.5 (68.8) |     | 18.5                  |                       |
|            | Cooling  | 104.8 (−10.7) | 140.7 (−4.9) |     | 1.42                  |                       |
| 4bCl        | Heating  |          | 171.1 (79.2) |     | 21.4                  |                       |
|            | Cooling  | 121.7 (−56.1) | 150.8 (−7.4) |     | 2.1                   |                       |
| 4cCl        | Heating  |          | 137.8 (19.7) |     | 167.7 (80.7)          | 22.0                  |
|            | Cooling  | 128.5 (−66.7) | 161.2 (−9.0) |     | 2.5                   |                       |
| 4dCl        | Heating  |          | 132.4 (14.2) |     | 164.3 (33.3)          | 9.1                   |
|            | Cooling  | 120.9 (−25.0) | 162.4 (−9.5) |     | 2.6                   |                       |
| 4eCl        | Heating  |          | 102.6 (5.8) | 159.9 (79.1) | 170.1 (10.2) | 2.8                   |
|            | Cooling  | 95.7 (−13.3) | 131.4 (−84.3) | 169.4 (−10.6) |                       | 2.9                   |
| 4aBr        | Heating  |          | 180.7 (77.9) |     | 20.6                  |                       |
|            | Cooling  | 148.3 (−61.3) | 174.0 (−6.1) |     | 1.6                   |                       |
| 4bBr        | Heating  |          | 177.4 (79.6) |     | 21.3                  |                       |
|            | Cooling  | 130.7 (−60.8) | 158.1 (−6.4) |     | 1.8                   |                       |
| 4cBr        | Heating  |          | 173.4 (76.3) |     | 20.5                  |                       |
|            | Cooling  | 134.0 (−54.9) | 166.9 (−7.2) |     | 1.9                   |                       |
| 4dBr        | Heating  |          | 75.5 (26.9) | 169.5 (83.4) | 175.9 (10.5) | 2.8                   |
|            | Cooling  | 55.3 (−6.2) | 134.2 (−68.6) | 171.1 (−9.4) |                       | 2.5                   |
| 4eBr        | Heating  |          | 139.1 (33.7) | 163.3 (59.3) | 178.7 (12.5) | 3.3                   |
|            | Cooling  | 92.1 (−4.0) | 137.3 (−70.8) | 175.9 (−8.3) |                       | 2.2                   |

**Table 6. Phase transition temperature (°C), associated enthalpies (kJ mol\(^{-1}\)) and entropy (\(\Delta S/R\)) of complexes 4aI-4eI.**

| Complex | Cr\(_1\) | Cr\(_2\) | SmA | I | \(\Delta S_{Cr,I}/R\) | \(\Delta S_{SmA,I}/R\) |
|---------|----------|----------|-----|-----|----------------------|-----------------------|
| 4aI     | Heating  |          | 188.9 (82.4) |     | 21.4                  |                       |
|         | Cooling  | 166.7\(a\) | 187.0 (−11.2) |     | 2.9                   |                       |
| 4bI     | Heating  |          | 181.1 (81.3) |     | 21.5                  |                       |
|         | Cooling  | 148.4 (−25.9) | 153.0 (−8.3) |     | 165.2 (−9.5)          |                       |
| 4cI     | Heating  |          | 163.5 (4.8) |     | 176.2 (72.4)          | 19.4                  |
|         | Cooling  | 71.7 (−38.9) | 152.3 (−67.3) |     | 173.6 (−10.7)         |                       |
| 4dI     | Heating  |          | 166.3 (39.7) | 174.8 (27.8) | 180.4 (12.9) | 3.4                   |
|         | Cooling  | 74.1 (−12.1) | 137.2 (−57.2) | 175.3 (−7.8) |                       | 2.1                   |
| 4eI     | Heating  |          | 154.3 (54.6) | 174.3 (25.4) | 184.1 (11.7) | 3.1                   |
|         | Cooling  | 140.3 (−24.8) | 147.8 (−12.2) | 181.5 (−9.4) |                       | 2.5                   |

**Note:** Cr\(_1\), crystal 1; Cr\(_2\), crystal 2; SmA, Smectic A; I, isotropic.

\(\Delta S/R\) Denotes transition temperature derived from polarising optical microscope equipped with hot stage.

A notable observation is the Cu(II) complexes 4dl-4eI display enantiotropic SmA phase as compared to monotropic SmA phase behaviour observed in their uncoordinated ligands 3dl-3eI. These findings indicate that the metal ion can stabilise the mesophase through the increase in the aspect ratio of aromatic core to terminal flexible chain.[23] Besides, the formation of Cu(II) complexes 4aI-4eI can also increase the colinearity and thus enhance the anisotropic properties of these non-linear ligands.[13,24] Figure 4 shows the summary of mesophase for ligands and their Cu(II) complexes.
dimensionless quantity $\Delta S/R$, where $\Delta S$ is obtained from $\Delta H/T$, $T$ is the corresponding phase transition in unit Kelvin, K, and $R$ is 8.314 JK$^{-1}$ mol$^{-1}$. From Table 1, the entropy values from isotropic to smectic phase for $1a16-1e16$ are relatively higher as compared to $1aBr-1eBr$. This observation suggests that $1a16-1e16$ is involved in the transition of isotropic to a more ordered SmC phase in which the entropy change is expressed in a dimensionless quantity of $\Delta S_{SmC,I}/R$. Besides, it can be inferred from Table 2 that the entropy values for all the Cu(II) complexes $2a16-2e16$ and $2aBr-2eBr$ are higher than their corresponding ligands. This is common because these entropy values are related to the transition between highly ordered crystal phase and liquid like isotropic phase.

$\Delta S_{Cr,I}/R$. From Tables 3–6, a general trend can be noted wherein the entropy values for the transition between crystal and isotropic phases, $\Delta S_{Cr,I}/R$, (Tables 4–6) are always higher in comparison with the transition between the SmA and isotropic phases, $\Delta S_{SmA,I}/R$ (Tables 3–6).

3.1.2 Thermal properties of Schiff bases 1, 3 and their complexes 2, 4

The correlation study between the thermal properties of uncoordinated ligands and their corresponding complexes are depicted in Figures 5 and 6. The clearing temperatures of all Cu(II) complexes increased by 28.7–44.4°C upon complexation. This implies that all the Cu(II) complexes reported in this study are thermally more stable than their uncoordinated ligands. A general trend can be noted in Figure 5, whereby ligands $1aBr-1eBr$ with bromo-substituent have higher clearing temperature than ligands $1a16-1e16$. A similar trend of thermal behaviour can also be observed in their corresponding Cu(II) complexes. The lower clearing temperature in ligands $1a16-1e16$ and their complexes $2a16-2e16$ could be due to the dilution of the mesogenic core resulting from the flexibility of the terminal end of the molecule. Furthermore, the long $n$-hexadecanoyloxy also cause the dispersion between the molecules and thus reduce the intermolecular interaction.[26]

Based on Figure 6, it can be deduced that the clearing temperatures of ligands 3 and their Cu(II) complexes 4 were greatly influenced by the polar terminal substituent group. The iodo-substituted ligands and their Cu(II) complexes have highest clearing temperature followed by bromo- and

\[ \Delta S_{Cr,I}/R \]

Figure 1. (colour online) Photomicrograph showing the SmC phase with broken fan-shaped texture of ligand $1d16$ at 130.4°C during the cooling process.

Figure 2. (colour online) Photomicrograph showing the SmA phase with focal conic fan-shaped texture of ligand $1dBr$ at 138.9°C during the cooling process.

Figure 3. (colour online) Photomicrograph showing the SmA phase with focal conic fan-shaped texture of Cu(II) complex $4dBr$ at 168.9°C upon cooling.
chloro-substituted ligands.[27,28] This observation could be rationalised by the variation in atomic sizes. Generally, the atomic sizes for halogen elements increase while descending the periodic table. Thus, the compounds containing iodine as substituent is inclined to the highest clearing temperature because it possesses the largest size among the halogens.[25,28] Furthermore, the large size of iodine atom is more polarisable because the valence electron in this atom is far apart from the nucleus. The existence of polarisable iodine atom could enhance the dipole–dipole and Van der Waals forces of attraction between the molecules and thus lead to higher clearing temperature.[28]
3.2 Chemical structure–thermal and mesomorphic property relationships

The homologous series of triazole-based bidentate Schiff bases 1aBr-1eBr and their corresponding Cu(II) complexes 2aBr-2eBr in Scheme 1 are compared to the structurally related ligands 3aBr-3eBr and their complexes 4aBr-4eBr in Scheme 2. Both series have almost identical molecular structure but with different positions of ortho-hydroxyl functional group which could possibly form intramolecular hydrogen bonding. The ortho-OH group in Scheme 1 is attached to the bromo-substituted aromatic ring, whereas the ortho-OH group in Scheme 2 is attached to another aromatic ring which is nearer to the triazole ring. It is found that even though both ligands display enantiotropic SmA phase but ligands 3aBr-3eBr (Scheme 2) show a lower thermal behaviour as illustrated in Figure 7. Based on the plot, it can be deduced that ligands 1aBr-1eBr with ortho-hydroxyl functional group attached to bromo-substituted aromatic ring can enhance the rigidity and increase the Van der Waals attractive forces between the molecules.[21]

Hence, it results in higher melting temperature for ligands 1aBr-1eBr. On the other hand, the ΔS_{SmA,I}/R values for ligands 1aBr-1eBr are higher than 2aBr-2eBr. The high ΔS_{SmA,I}/R values reveal that the ordering of the ligands 1aBr-1eBr with respect to the SmA and isotopic transition is higher than ligands 1aBr-2eBr.[29]

Comparison studies reveal that Cu(II) complexes 4aBr-4eBr possess lower transition temperature and exhibit SmA phase, whereas Cu(II) complexes 2aBr-2eBr are non-mesomorphic. These differences could be due to the ortho-OH group which is attached to the bromo-substituted aromatic ring in ligands 1aBr-1eBr involved in the coordination with the Cu(II) ion.

However, in the absence of ortho-OH group in the bromo-substituted aromatic ring, the ligands 3aBr-3eBr established the coordination with Cu(II) ion. The different positions of ortho-OH group that causes the structural orientation for Cu(II) complexes 2aBr-2eBr do not favour the mesophase formation.[14] Hence, the suppression of mesophase and difference in clearing temperature could be attributed to the different coordination geometry between these two Cu(II) complexes.[30]

4. Conclusion

Two series of heterocyclic ligands and their Cu(II) complexes have been synthesised and their mesomorphic properties were analysed. All the targeted compounds were elucidated by elemental analysis, FT-IR, ^1H-NMR and UV–visible spectroscopic methods. Present study show that all the non-linear triazole-based ligands were either enantiotropic or monotropic, whereas not all Cu(II) complexes exhibit liquid crystalline properties. The non-colinearity of the iodo-substituted ligands has led to the formation of non-stable SmA phase. However, their Cu(II) complexes enhanced the colinearity and thus formed a stable monotropic SmA phase which are reproducible. Thermal behaviour studies show that the iodo-substituted ligands and complexes have the highest clearing temperature as compared to chloro- and bromo-substituted ligands and their related complexes.

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Supplemental data

Supplemental data for this article can be accessed here.

References

[1] Gallardo H, Bortoluzzi AJ, De Oliveira Santos DMP. Synthesis, crystalline structure and mesomorphic properties of new liquid crystalline 1,2,3-triazole derivatives. Liq Cryst. 2008;35:719–725. doi:10.1080/02678290802120307.
[2] Srividhya D, Manjunathan S, Thirumaran S, Saravanan C, Senthil S. Synthesis and characterization of [1,2,3]-triazole containing liquid crystals through click reaction. J Mol Struct. 2009;927:7–13. doi:10.1016/j.molstruc.2009.01.035.
[3] Frizon TE, Dal-Bó AG, Lopez G, Silva Paula MM, Silva L. Synthesis of luminescent liquid crystals derived from gallic acid containing heterocyclic...
1,3,4-oxadiazole. Liq Cryst. 2014;41:1162–1172. doi:10.1080/02678292.2014.909354.

[4] Balamurugan S, Yeap GY, Kamil Mahmood WA. Calamitic liquid crystals of 1,2,3-triazole connected to azobenzene: synthesis, characterisation and anisotropic properties. Liq Cryst. 2014;41:776–783.

[5] Benbayer C, Besbes SS, Grelet E, Derdour A. Structure–property study of new [1,2,3]-triazole liquid crystalline derivatives. Liq Cryst. 2013;40:1520–1528. doi:10.1080/02678292.2013.822111.

[6] Uppal BS, Booth RK, Ali N, Lockwood C, Rice CR, Elliott PP. Synthesis and characterisation of luminescent rhenium tricarbonyl complexes with axially coordinated 1,2,3-triazole ligands. Dalton Trans. 2011;40:7610. doi:10.1039/c1dt10634a.

[7] Yeap G-Y, Heng B-T. Mesogenic copper(II) complexes with [1,2,3]-triazole-based bidentate Schiff bases. J Chem Sci. 2014;126:247–254. doi:10.1007/s12039-013-0545-0.

[8] Velasco BE, Fuentes A, Gonzalez C, Corona D, Orozco IG, Cuevas-yañez E. Synthesis of (tetrahydrofuranyloxy)alkanes. Liq Cryst. 2011;38:2966–2973. doi:10.1080/0267829010130750.

[9] Velasco BE, Fuentes A, Gonzalez C, Corona D, Orozco IG, Cuevas-Yañez E. Synthesis of (tetrahydrofuranyloxy)alkanes. Liq Cryst. 2011;38:2966–2973. doi:10.1080/0267829010130750.

[10] Rezvani Z, Divband B, Abbasi AR, Nejati K. Liquid crystalline properties of binucleating Schiff-base ligands with long side chains and their binuclear Cu(II) and Ni(II) complexes. Mol Cryst Liq Cryst. 2005;432:47–57. doi:10.1080/0267829050013972.

[11] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[12] Mun Jung B, Huang YD, Chang JY. Preparation of discotic metallomesogens based on phenacylpyridines showing room temperature columnar phases. Liq Cryst. 2009;37:85–92. doi:10.1080/02678290903390940.

[13] Cardinaels T, Ramaekers J, Guillon D, Donnio B, Binnemans K. Novel stationary phase for complexation gas chromatography originating from ionic liquid and metallomesogens. J Chromatogr A. 2008;1215:177–184. doi:10.1016/j.chroma.2008.11.018.

[14] Velasco BE, Fuentes A, Gonzalez C, Corona D, Orozco IG, Cuevas-Yañez E. Synthesis of (tetrahydrofuranyloxy)alkanes. Liq Cryst. 2011;38:2966–2973. doi:10.1080/0267829010130750.

[15] Velasco BE, Fuentes A, Gonzalez C, Corona D, Orozco IG, Cuevas-Yañez E. Synthesis of (tetrahydrofuranyloxy)alkanes. Liq Cryst. 2011;38:2966–2973. doi:10.1080/0267829010130750.

[16] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[17] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[18] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[19] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[20] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[21] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[22] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[23] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[24] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[25] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[26] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.

[27] Prasad D, Aggarwal N, Kumar R, Nath M. Synthesis of novel heteroarenes based 1,2,3-triazole liquid crystals. Liq Cryst. 2005;32:667–671. doi:10.1080/0267829050013973.