

Article

Synthesis and Mesomorphic Studies of Copper(II) with Carboxylate and N-Donor Ligands

Lailatun Nazirah Ozair^{1,a}, Farhanah Mohd Redwan¹, Bohari Mohd. Yamin¹, Farah Aini Azizi¹, Muhammad Syahmi Mustafani¹, Muhammad Syafiq Nasir¹, Nurul Husna Hasan¹, Mohd Adib Yahya¹

¹Faculty of Science and Technology, Universiti Sains Islam Malaysia (USIM), Nilai 71800, Negeri Sembilan, Malaysia
E-mail: ^alailatunnazirah@usim.edu.my

Abstract— Metal containing liquid crystals also known as metallomesogens is an orientationally ordered liquid that combines properties of both crystalline state and liquid state. Three linear and one branched alkyl chain complexes of general formula $[\text{Cu}_2(\text{RCOO})_4(\text{X})_2]$, where $\text{R} = \text{CH}_3(\text{CH}_2)_{13}$ (Complex 1, Complex 2), $p\text{-CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4$ (Complex 3) and $\text{CH}_3(\text{CH}_2)_7\text{CH}[(\text{CH}_2)_5\text{CH}_3]$ (Complex 4), $\text{X} = \text{pyridine}$ or 2,2-bipyridine were prepared. The single crystal X-ray crystallography of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{py})_2]$ (Complex 1) shows dinuclear complexes with each square pyramidally Cu(II) centre was bridged by four carboxylate molecules and a pyridine molecule. For all complexes, the IR spectra gave the $\Delta\nu_{\text{COO}}$ values in the range of 164 - 240 cm^{-1} , suggesting two binding modes of the alkylcarboxylate ligands. The UV-vis spectra shows a broad $d-d$ band at $\lambda_{\text{max}} \sim 664 - 699 \text{ nm}$ ($\epsilon_{\text{max}} \sim 55 - 341 \text{ M}^{-1} \text{ cm}^{-1}$), indicating that the distorted square pyramidal geometry at Cu(II). From the results of differential scanning calorimetry (DSC) and optical polarizing microscopy (OPM), complexes 1-4 exhibited liquid crystal mesophases.

Keywords— Copper(II) carboxylate; Structural; Liquid crystals.

I. INTRODUCTION

Copper (Cu) is one of transition metal located on the first row of the transition metal. Transition metal from this row is cheaper, relatively easy to handle, readily available in a pure state, and simplicity in analyzing method. Transition metal has their own properties towards the electronic conductivity, thermal stability, colour and magnetic.

Basically, copper has high thermal and electrical conductivity, and because of its unique properties copper becomes one of the important metals. Metal containing liquid crystals is known as metallomesogens [1]. Liquid crystal is an intermediate phase of solid and liquid. Fig. 1 shows the different arrangement of solid, liquid crystal and liquid.

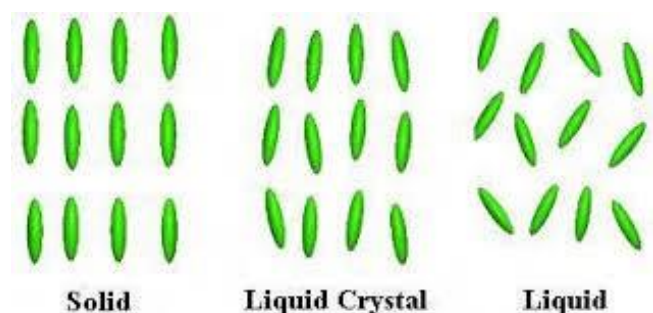


Fig. 1 Molecular arrangement between solid, liquid crystal and liquid [2]

The study of metallomesogens is considered new in the field of liquid crystals. Liquid crystals or mesogens are the

material, which exhibit mesomorphic properties. Liquid crystals are 'orientationally ordered' liquids that combine properties of both crystalline state and liquid state.

The specialties of liquid crystal properties are fluidity, molecular arrangement and self-healing, which can design multifunctional materials. Hence, by combining the properties between both transition metals and liquid crystals can create and design multifunctional materials.

In previous research, copper(II) acetate hydrate $[\text{Cu}_2(\text{MeCO}_2)_4(\text{H}_2\text{O})_2]$ is the first tetracarboxylate bridged copper(II) dimer structure that have been reported by Van Niekerk and Schoening in 1953 [3]. Since the discovery of $[\text{Cu}_2(\text{MeCO}_2)_4(\text{H}_2\text{O})_2]$ as the first copper(II) carboxylate, the chemists in production used numerous of the different carboxylate groups and due to its excellent properties, it had attracted the chemists to explore this field.

Nowadays, metal complexes have been studied in order to improve the efficiency and develop optoelectronic devices with low cost of production. Optoelectronic devices are those electronic devices that able to operate both electric currents and light. At this time, optoelectronic devices are found in various applications in the medical field, telecommunications, military services, and automatic control systems. The needs of suitable complexes as the materials in the devices are important to improve its efficiency. Copper complex has potential to give significant function that can be used as materials to operate in optoelectronic devices [4].

Optoelectronics is an interesting branch of electronics that combines both optics and electronics. Organic light-emitting devices (OLEDs) is one of the optoelectronic devices.

Iridium(III) complexes is a well-established light-emitting materials used in this devices. Iridium complexes have special properties, such as shorter excited state lifetime and high photoluminescence quantum yield (PLQY) [4]. Iridium complexes were recognized as more favorable candidates to replace platinum complexes. Nevertheless, iridium is one of the most expensive metals in the world and very limited availability. Although iridium is highly stable, it only can produce lower reaction yield.

Metal complexes played an important role and property in a variety of applications nowadays. The examples of applications are in the area of fungicidal activities [5], wood preservatives [6], gas occlusion compounds, pharmaceuticals, catalysts, switching and sensing in different temperature regimes, thermoelectric, potential photoluminescence materials and facile formation of thin films.

Not only that, copper(II) carboxylates also have been applied as anticorrosive materials [7], precursors in the synthesis of metal-organic frameworks [8], and as molecular templates in the synthesis of semiconductor nanorods [9]. Furthermore, in recent years, there has been an increasing interest in the use of these complexes due to their wide range of applications [10].

Many researchers from various fields are attracted in the studies of the copper(II) complexes because of its unique properties. Most of the metallomesogens have high melting point, usually higher than 523 K [11]. In this research, low melting of copper(II) complexes were synthesized.

This paper presents the syntheses and characterization of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{py})_2]$ (**1**), $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{bpy})_2]$ (**2**), $[\text{Cu}_2(p\text{-CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4\text{COO})_4(\text{bpy})_2]$ (**3**) and $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)_5\text{CH}_3\text{COO})_4(\text{py})_2]$ (**4**).

Complex **1** was single crystals and its structure was determined by X-ray crystallography and H-NMR spectroscopy. The main objectives of this paper were: (a) to deduce the structures, and (b) to compare the thermal and mesomorphic properties of the complexes formed.

II. EXPERIMENTAL

A. Syntheses

$\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$ (1.50 g; 6.19 mmol), ethanol (20 mL), Na_2CO_3 (0.32 g; 3.09 mmol) were magnetically stirred and heated at 60 °C for 30 minutes. The mixture was cool to room temperature. Then, half volume of the solvent was removed using the rotary evaporator. A white solid of $\text{CH}_3(\text{CH}_2)_7\text{COONa}$ was obtained after a week. The product was filtered and washed with distilled water before drying overnight. Yield: 1.595 g (97%). IR (neat, cm^{-1}): 2916 (s), 2854 (m), 1558 (s), 1435 (m).

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.32 g, 1.90 mmol) was added portionwise to a solution of $\text{CH}_3(\text{CH}_2)_{13}\text{COONa}$ (1.00 g, 3.79 mmol) in aqueous $\text{C}_2\text{H}_5\text{OH}$ (1:2 v/v, 30 ml) and heated for 30 min, and then left to cool to room temperature. The blue solid precursor of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4]$ was filtered off, washed with $\text{C}_2\text{H}_5\text{OH}$ and dried. Yield: 0.99 g (67%). IR (neat, cm^{-1}): 2916 (s), 2854 (m), 1589 (s), 1450 (m).

$[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{py})_2]$ (**1**): Pyridine (73.80 μL , 0.92 mmol) was added to the $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4]$ solution (0.50 g, 0.48 mmol) in CHCl_3 -MeOH solution (1:2

v/v, 30 ml). The mixture was heated for another 30 min and then left to cool to room temperature. The green crystals of Complex **1** were filtered off, washed with distilled water and dried. Yield: 0.34 g (59%). IR (neat, cm^{-1}): 2916 (s), 2854 (m), 1620 (s), 1450 (m), 1512(m), 1311 (w).

$[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{bpy})_2]$ (**2**): The procedure was similar as **1**, using 2,2'-bipyridine (0.20 g, 1.28 mmol) and $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4]$ (0.70 g, 0.64 mmol). The product was a dark blue solid. Yield: 0.78 g (87%). IR (neat, cm^{-1}): 2919 (s), 2855 (m), 1625 (s), 1451/1385 (m), 1559 (m), 1285 (w).

$[\text{Cu}_2(p\text{-CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4\text{COO})_4(\text{bpy})_2]$ (**3**): *p*- $\text{HOC}_6\text{H}_4\text{COOCH}_3$ (5.01 g; 33.00 mmol), K_2CO_3 (4.55 g; 33.00 mmol), KI (0.25 g; 1.50 mmol) and $\text{CH}_3(\text{CH}_2)_{14}\text{Br}$ (9.59 g; 33.00 mmol) were added in 200 ml DMF and reflux for 12 hours. The solid was filtered out and washed with water and ethanol before further dissolved in CHCl_3 and dried using MgSO_4 anhydrous. The white solid of *p*- $\text{CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4\text{COOCH}_3$ was collected. Yield: 6.39 g (54%). $^1\text{H NMR}$ (CDCl_3) δ /ppm: 7.99 (d, 2H), 6.93 (d, 2H), 4.02 (t, 3H), 3.90 (s, 3H), 1.82 (m, 2H), 1.48 (m, 2H), 1.28 (m, 22H), 0.90 (t, 2H). IR (neat, cm^{-1}): 2919 (s), 2854 (m), 1607 (s), 1441 (s), 1266 (s).

Potassium hydroxide (0.62 g; 11.00 mmol) was added to the product above (4.00 g; 11.00 mmol) in hot ethanolic solution and refluxed for 4 hours. The white solid of *p*- $\text{CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4\text{COOK}$ was cooled to room temperature and filtered. Yield: 3.37 g (79%). IR (neat, cm^{-1}): 2920 (s), 2856 (m), 1602 (s), 1546 (s), 1399 (s).

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.21 g; 4.84 mmol) was added to *p*- $\text{CH}_3(\text{CH}_2)_{14}\text{OC}_6\text{H}_4\text{COOK}$ (3.75 g; 9.69 mmol) in ethanol:water (1:1 v/v, 100 ml). The mixture was heated for 30 minutes and the blue powder was filtered hot. Yield: 1.66 g (46%). IR (neat, cm^{-1}): 2918 (s), 2855 (m), 1603 (s), 1434 (s), 1256 (s).

2,2'-Bipyridine (0.08 g; 0.53 mmol) was added to the blue powder (0.45 g; 0.27 mmol) which was immersed in ethanol. The mixture was heated for about 1 hour. The blue solid of **3** was collected. Yield: 0.33 g (67%). IR (neat, cm^{-1}): 2920 (s), 2856 (m), 1599 (m), 1543 (m), 1379/1311 (s), 1248 (s).

$[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)_5\text{CH}_3\text{COO})_4(\text{py})_2]$ (**4**): The procedure was similar as for **1**, using pyridine (211.00 μL , 2.6 mmol) and $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)_5\text{CH}_3\text{COO})_4]$ (1.50 g, 1.30 mmol). The product was a dark green viscous solid. Yield: 0.33 g (58%). IR (neat, cm^{-1}): 2928 (s), 2859 (m), 1609 (m), 1546 (s), 1443 (m), 1327 (m).

B. Crystallographic Data Collection and Structural Determination

Single-crystal X-ray diffraction data were collected at 293(2) K on a Bruker SMART APEX II CCD fitted with Mo $\text{K}\alpha$ radiation so that θ_{max} was 27.5°. The data set was corrected for absorption based on multiple scans and reduced using standard methods [12]. The structures were solved by direct methods with SHELXS97 [13] and refined by a full-matrix least-squares procedure on F2 using SHELXL97 with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(\text{Fo}^2) + a\text{P}^2 + b\text{P}]$, where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$. All hydrogen atoms were included in the final refinement in their calculated positions.

C. Physical Measurements

Samples for $^1\text{H-NMR}$ analysis were dissolved in CDCl_3 before being analysed on JEOL FT-NMR Lambda 400 MHz spectrometer. FTIR spectra was recorded on a Varian 3100 FTIR Excalibur Series equipped with a diamond attenuated total reflectance attachment from 4000 cm^{-1} to 400 cm^{-1} . UV-visible spectra was recorded on a Varian Cary 50 Conc spectrometer.

Differential scanning calorimetry (DSC) was analysed in an inert N_2 atmosphere at scan rate and flow rate of $10\text{ cm}^3\text{ min}^{-1}$ and $10\text{ }^\circ\text{C min}^{-1}$ respectively. The onset temperatures were quoted for all peaks observed. Polarising optical microscopy (POM) was carried out on an Olympus BX51 microscope equipped with a Mettler Toledo FP90 central processor and Mettler Toledo FP82HT hot stage. The heating and cooling rates were $10\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C min}^{-1}$, respectively, and the magnification was 10x.

III. RESULT AND DISCUSSIONS

A. Molecular Structures of 1

$[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4]$ reacted with 2,2'-bipyridine (bpy) to form dinuclear complex of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{py})_2]$ (**1**). This complex was single crystals and its data and structure refinement details are shown in Table I, while selected bond lengths and angles are shown in Table II.

TABLE I
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT
DETAILS FOR **1**

Empirical formula	$\text{C}_{70}\text{H}_{126}\text{Cu}_2\text{N}_2\text{O}_8$
Formula weight	Formula weight
Temperature (K)	103(2)
Crystal system	Triclinic
Space group	P-1
Unit cell dimension	$a = 8.0489(5)\text{ \AA}$ $\alpha = 84.442(4)^\circ$ $b = 10.2024(6)\text{ \AA}$ $\beta = 82.378(4)^\circ$ $c = 21.8671(13)\text{ \AA}$ $\gamma = 86.026(4)^\circ$ $V (\text{\AA}^3) 1768.55(19)$
Z	1
ρ (calcd) (g cm^{-3})	1.174
μ (mm^{-1})	0.073
F (000)	682
Crystal size	$0.260 \times 0.220 \times 0.030\text{ mm}^3$
θ range ($^\circ$)	2.876 to 25.156
Index ranges	$-9 < h < 9, -12 < k < 12, 26 < l < 26$
Reflections collected	71969
Independent reflections, Rint	6305, 0.4761
Completeness to θ	99.4 %
Data / restraints / parameters	6305 / 0 / 372
Goodness-of-fit on F2	1.041
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0828, wR2 = 0.1183$
R indices (all data)	$R1 = 0.1759, wR2 = 0.1448$

TABLE II
SELECTED BOND LENGTHS (\AA) AND ANGLES ($^\circ$) FOR **1**

Bond length	Angle
$\text{Cu}(1)\text{-O}(3) 1.960(3)$	$\text{O}(3)\text{-Cu}(1)\text{-O}(2) 89.55(14)$
$\text{Cu}(1)\text{-O}(2) 1.967(3)$	$\text{O}(3)\text{-Cu}(1)\text{-O}(4) 168.17(13)$
$\text{Cu}(1)\text{-O}(4) 1.967(3)$	$\text{O}(2)\text{-Cu}(1)\text{-O}(4) 87.61(14)$
$\text{Cu}(1)\text{-O}(1) 1.977(3)$	$\text{O}(3)\text{-Cu}(1)\text{-O}(1) 88.71(14)$
$\text{Cu}(1)\text{-N}(1) 2.153(4)$	$\text{O}(2)\text{-Cu}(1)\text{-O}(1) 168.81(13)$
$\text{Cu}(1)\text{-Cu}(1) 2.6266(13)$	

Based on the data in Table I, **1** crystallized in P-1 space group with the triclinic crystal system. Unit cell dimensions were $a = 8.0489(5)\text{ \AA}$, $b = 10.2024(6)\text{ \AA}$, $c = 21.8671(13)\text{ \AA}$, $\alpha = 84.442(4)^\circ$, $\beta = 82.378(4)^\circ$, $\gamma = 86.026(4)^\circ$, $Z = 1$ and $V = 1364(3)\text{ \AA}^3$.

Structure in Fig. 2 shows one N atom attached to each of the copper(II) centre. At this coordination was supported by the data obtained in Table II, $\text{Cu-N1} = 2.153(5)\text{ \AA}$ while four O atoms from bridging bidentate $\text{CH}_3(\text{CH}_2)_{13}\text{COO}^-$ ligands are $\text{Cu}(1)\text{-O}(3) = 1.960(3)\text{ \AA}$, $\text{Cu}(1)\text{-O}(2) = 1.967(3)\text{ \AA}$, $\text{Cu}(1)\text{-O}(4) = 1.967(3)\text{ \AA}$ and $\text{Cu}(1)\text{-O}(1) = 1.977(3)\text{ \AA}$. The Cu-Cu separation within the dimer recorded at $2.6266(13)\text{ \AA}$.

Normally, paddle-wheel structure of Cu-Cu bond for copper(II) complexes is at about 2.6 \AA [14].

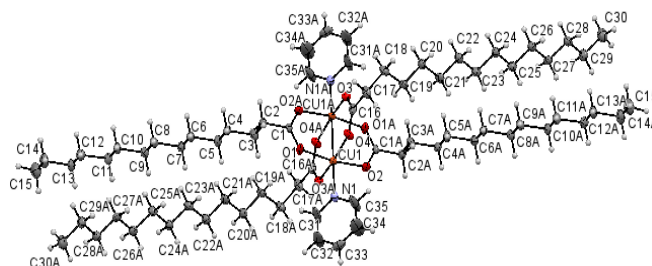


Fig. 2 Crystal structure and packing of Complex 1

B. IR and UV-vis Spectroscopies

FTIR spectrum for **1** (Fig. 3) shows the presence of all expected functional groups as shown in Table IV. The FTIR data also supported the molecular structure generated from the single crystal where it showed two strong peaks at 1620 cm^{-1} (ν_{asymCOO}) and 1450 cm^{-1} (ν_{symCOO}). Accordingly, the Δ value ($\Delta = \nu_{\text{asymCOO}} - \nu_{\text{symCOO}} = 170\text{ cm}^{-1}$) as shown in Table III was in a good agreement with the bridging bidentate binding mode of the carboxylate ligands [14]. Similar results observed for **4**. However, for **2** and **3**, the Δ values showed that both complexes undergo chelating and monodentate bridging carboxylate ligands [14].

TABLE III
INSTRUMENTAL DATA FOR COMPLEX **1** – **4**

Complex	IR $\Delta^\circ/\text{cm}^{-1}$	UV-vis λ/nm ($\epsilon/\text{M}^{-1}\text{ cm}^{-1}$)	DSC $T/^\circ\text{C}$ ($\Delta H/\text{kJ mol}^{-1}$)
1	170	679 (271)	96 (+91) Cr-M 79 (-80) I-M 61.5 (-23) M-Cr
2	240, 174	685 (341)	115 (+52) Cr-M 157 (+33) M-I 118 (-1) I-M 43 (-12) M-Cr
3	164, 232	720 (55)	100 (+83) Cr-M 123 (+32) M-I 115 (-4) I-M
4	156	670 (64)	41 (+1) Cr-M 171 (+5) M-I 188 (-9) I-M

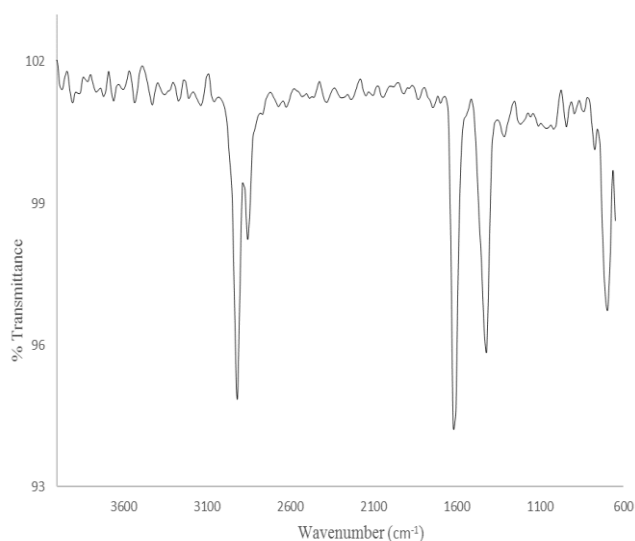


Fig. 3 FTIR spectrum for complex 1

Electronic absorption spectra at 679 nm ($\epsilon_{\max} = 271 \text{ M}^{-1} \text{ cm}^{-1}$) and 670 nm ($\epsilon_{\max} = 64 \text{ M}^{-1} \text{ cm}^{-1}$) for **1** (Fig. 4) and **4**, respectively correspond to the *d-d* forbidden bands. Hence, it is suggested the geometry of the complexes was square pyramidal at each Cu(II) centres [15]. The square pyramidal geometry was also agreed with the X-ray crystallography data.

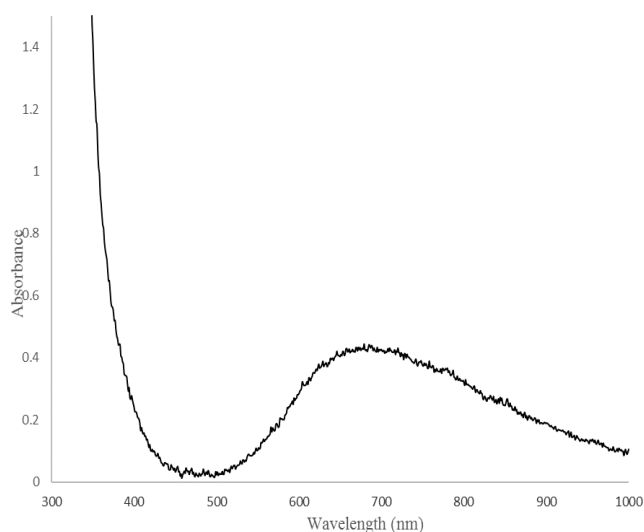


Fig. 4 UV-Vis spectrum for complex 1

Similar broad band observed for **2** and **3** at 685 nm and 720 nm showed both complexes underwent a distorted octahedral Cu(II) geometry, where electronic transitions arose from ${}^2B_{1g}$ to E_{1g} , ${}^2B_{2g}$ and ${}^2A_{1g}$ [16]. The later geometry suggested due to the *syn-anti* and chelating carboxylate ligands with chelating 2,2'-bipyridine bonded to each Cu(II) centres [14].

C. Mesomorphic Studies

DSC and POM were done to investigate the mesomorphic studies for all complexes. Both heating and cooling modes recorded from the DSC were tabulated in Table III. Complex

2 showed two broad endothermic peaks at 115 °C ($\Delta H = +52 \text{ kJ mol}^{-1}$) and 157 °C ($\Delta H = +33 \text{ kJ mol}^{-1}$) on heating, and two exothermic peaks at 118 °C ($\Delta H = -1 \text{ kJ mol}^{-1}$) and 43 °C ($\Delta H = -12 \text{ kJ mol}^{-1}$) on cooling where these traces were recorded in the temperature range of 30 – 200 °C.

When viewed under POM, **2** started to melt at 110 °C and started to clear to isotropic liquid at about 156 °C. Upon cooling from isotropic liquid, an optical texture was observed at 115 °C. Combining the above results, it is suggested that **2** behaved as thermotropic metallomesogens.

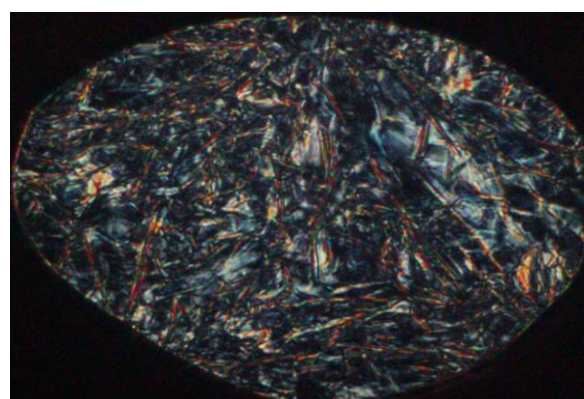
TABLE IV
IR DATA FOR COMPLEX 1

Functional Group	Wavelength, cm^{-1}
CH_2 (asym)	2916
CH_2 (sym)	2854
COO (asym)	1620
COO (sym)	1450
C=C (aromatic)	1512
C-N	1311

All complexes showed mesomorphic properties. Similar optical textures were observed for **1** and **4** (Fig. 5), probably due to the similar molecular structure. However, **4** (Fig. 6) showed the lowest melting temperature supported with the presence of the long branched alkyl carboxylate ligands [17].

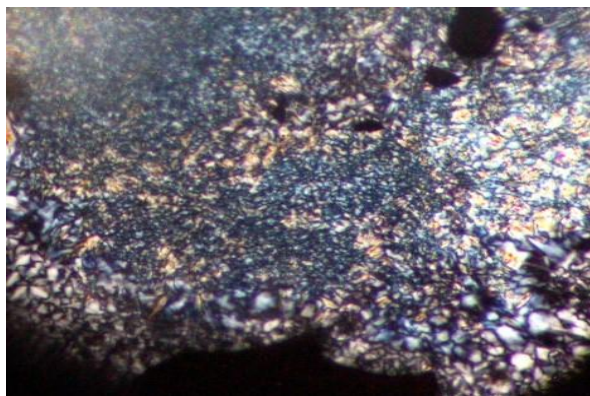


(a)



(b)

Fig. 5 Optical texture of (a) Complex 1 and (b) Complex 2



(a)



(b)

Fig. 6 Optical texture for (a) complex **3** at 120°C and (b) **4** at 89°C

IV. CONCLUSIONS

$[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4]$ reacted with pyridine and 2,2'-bipyridine to form complexes $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{py})_2]$ (**1**) and $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{13}\text{COO})_4(\text{bpy})_2]$ (**2**) respectively. **1** was crystallized in triclinic P-1 space group, where the Cu(II) centres were bonded to four carboxylato ligands at the equatorial positions and one pyridine at the axial. Similar characterization observed for **4** proposing it underwent similar molecular structure as **1**.

However, **2** and **3** are proposed to have distorted octahedral geometry at each Cu(II) centres, where two carboxylato ligands bonded as *syn-anti* bridging modes, one chelating carboxylato ligand and two chelating nitrogen from the 2,2'-bipyridine. In addition, all complexes suffered structural changes on cooling to become dinuclear thermotropic metallomesogenic complexes.

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