CHAPTER 3 EXPERIMENTAL

3.1 Introduction

This research was based on the findings that a new Schiff base, H₂salnon (Figure 3.1) reacted with metal(II) acetates to form a dinuclear magnetic complex with Cu(II) ion, but mononuclear magnetic complexes with Ni(II) and Co(II) ions [1].

Figure 3.1 Crystal structure of H₂salnon

Hence, the initial objectives of this research were to find out the effect of changing: (a) the alkyl chain length in the Schiff bases, and (b) metal(II) acetates to metal(II) hexadecanoates, on the nuclearity and other properties (especially mesomorphism and spin crossover) of the metal(II) complexes (Cu(II), Ni(II), Co(II), Fe(II)) formed. The Schiff bases chosen were H₂saloct (8-carbon chain) and H₂saldec (10-carbon chain) shown in Figure 3.2.

Figure 3.2 Structural formula of: (a) H₂saloct (n = 8, L₁); H₂saldec (n = 10, L₂); and (b) H₂salpen (L₃)
The next objective of the research was to increase the nuclearity of the magnetic complexes, which is desirable in molecular magnetism. This was done based on the literature report that a Schiff base ligand formed a linear trinuclear complex with nickel(II) acetate or nickel(II) perchlorate (Figure 3.3) [2].

![Crystal structure of \([\text{Ni}_3(\text{salpen})_2(\text{OAc})_2(\text{H}_2\text{O})_2]\cdot4\text{H}_2\text{O}\)](image)

**Figure 3.3** Crystal structure of \([\text{Ni}_3(\text{salpen})_2(\text{OAc})_2(\text{H}_2\text{O})_2]\cdot4\text{H}_2\text{O}\)

The project involved the syntheses of the Schiff bases, ligand \(H_2L1\), \(H_2L2\) and \(H_2L3\) with metal(II) complexes, deducing their chemical formulas by elemental analysis, \(^1\text{H}-\text{nuclear magnetic resonance spectroscopy}, \) Fourier transform infrared spectroscopy, UV-visible spectroscopy, thermal stability by differential scanning calorimetry and thermogravimetry, mesomorphism by polarized optical microscopy, and magnetic properties by room-temperature magnetic susceptibility balance and variable-temperature superconducting interference device magnetometry.

### 3.2 Chemicals

The main chemicals used in the research are listed in **Table 3.1**.
Table 3.1 Chemicals used in the research

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical Formula</th>
<th>Formula weight (g mol$^{-1}$)</th>
<th>Purity (%)</th>
<th>Company</th>
</tr>
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<tbody>
<tr>
<td>2-Hydroxybenzaldehyde</td>
<td>2-HOC$_6$H$_4$CHO</td>
<td>122.12</td>
<td>99</td>
<td>Merck</td>
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<tr>
<td>1,8-Diaminoctane</td>
<td>H$_2$N(CH$_2$)$_3$NH$_2$</td>
<td>144.26</td>
<td>98</td>
<td>Merck</td>
</tr>
<tr>
<td>1,10-Diaminododecane</td>
<td>H$_2$N(CH$<em>2$)$</em>{10}$NH$_2$</td>
<td>172.31</td>
<td>97</td>
<td>Acros</td>
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<tr>
<td>1,3-Diaminopentane</td>
<td>H$_2$N(CH$_2$)$_2$CH(NH$_2$)CH$_2$CH$_3$</td>
<td>102.18</td>
<td>97</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Hexadecanoic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{14}$COOH</td>
<td>256.42</td>
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<td>Aldrich</td>
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<tr>
<td>Sodium carbonate</td>
<td>Na$_2$CO$_3$</td>
<td>105.99</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Copper(II) chloride dihydrate</td>
<td>CuCl$_2$.2H$_2$O</td>
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<td>98</td>
<td>R&amp;M Chemicals</td>
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<tr>
<td>Nickel(II) chloride hexahydrate</td>
<td>NiCl$_2$.6H$_2$O</td>
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<td>98</td>
<td>R&amp;M Chemicals</td>
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<tr>
<td>Cobalt(II) chloride hexahydrate</td>
<td>CoCl$_2$.6H$_2$O</td>
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<td>99</td>
<td>R&amp;M Chemicals</td>
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<tr>
<td>Iron(II) sulphate heptahydrate</td>
<td>FeSO$_4$.7H$_2$O</td>
<td>278.02</td>
<td>99</td>
<td>Merck</td>
</tr>
</tbody>
</table>

3.3 Syntheses

The syntheses involved step-wise and one-pot reactions.

3.3.1 Schiff bases

(a) $H_2L1$

2-Hydroxybenzaldehyde (4.88 g; 40 mmol) was added to a solution of 1,8-diaminoctane (2.89 g; 20 mmol) in ethanol (100 mL), followed by a few drops of glacial acetic acid to act as a catalyst. The reaction mixture was heated under reflux for 3 hours, and the yellow solution formed was left overnight at room temperature. The yellow crystals formed were filtered, washed with cold ethanol and left to dry at room temperature. The yield was 5.37 g (76.1%). *Anal. Calc.* for C$_{22}$H$_{28}$N$_2$O$_2$ (FW, 352.47 g mol$^{-1}$): C, 75.0; H, 8.0; N, 8.0. *Found:* C, 75.3; H, 7.9; N, 8.2%.

(b) $H_2L2$

The procedure was the same as in 3.3.1(a), replacing 1,8-diaminoctane with 1,10-diaminododecane (3.45 g; 20 mmol). The product was yellow crystals and the yield
was 5.64 g (74.2%). *Anal.* Calc. for C\textsubscript{24}H\textsubscript{32}N\textsubscript{2}O\textsubscript{2} (FW, 380.52 g mol\textsuperscript{-1}): C, 75.8; H, 8.5; N, 7.4. Found: C, 75.5; H, 8.8; N, 7.3%.

\(c\) \(H_2L3\)

The procedure was the same as in 3.3.1(a), replacing 1,8-diaminoctane with 1,3-diaminopentane (2.04 g; 20 mmol). The solvent was removed on a rotary evaporator to give a viscous yellow liquid. The yield was 5.27 g (84.8%). *Anal.* Calc. for C\textsubscript{19}H\textsubscript{22}N\textsubscript{2}O\textsubscript{2} (FW, 310.39 g mol\textsuperscript{-1}): C, 73.5; H, 7.1; N, 9.0. Found: C, 72.8; H, 7.0; N, 8.8%.

3.3.2 \([M(CH_3(CH_2)_{14}COO)_2]\)

\((a)\) \(CH_3(CH_2)_{14}COONa\)

CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{14}COOH (24.68 g; 96.2 mmol) was added portion wise to an aqueous solution of Na\textsubscript{2}CO\textsubscript{3} (5.10 g; 48 mmol) in distilled H\textsubscript{2}O. The cloudy mixture formed was heated and stirred on a hot plate for 30 minutes. The solid formed was then filtered and dried in a warm oven (60 °C) overnight. The yield was 23.96 g (89.5%). *Anal.* Calc. for C\textsubscript{16}H\textsubscript{31}O\textsubscript{2}Na (FW, 278.41 g mol\textsuperscript{-1}): C, 69.0; H, 11.2. Found: C, 68.6; H, 11.4%.

\((b)\) \([Cu(CH_3(CH_2)_{14}COO)_2]\)

CuCl\textsubscript{2}.2H\textsubscript{2}O (3.12 g; 18.3 mmol) was added to a hot solution of CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{14}COONa (10.23 g; 36.7 mmol) in ethanol (100 mL). The mixture was heated for another 30 minutes. A fine greenish-blue powder formed was filtered under suction, washed with distilled water followed by ethanol, and then dried in a warm oven (60 °C). The yield was 4.52 g (43.0%). *Anal.* Calc. for C\textsubscript{32}H\textsubscript{62}CuO\textsubscript{4} (FW, 574.38 g mol\textsuperscript{-1}): C, 66.9; H, 10.9. Found: C, 66.1; H, 11.0%.
(c) \([\text{Ni(C}_3\text{H}_3(\text{CH}_2)_{14}\text{COO})_2]\)

NiCl\(_2\cdot6\text{H}_2\text{O}\) (2.17 g; 16.74 mmol) was added to a hot ethanolic solution of \(\text{CH}_3(\text{CH}_2)_{14}\text{COONa}\) (5.12 g; 18.3 mmol). The mixture was then further heated for 30 minutes. A fine light green powder formed was filtered under suction, washed with distilled water followed by ethanol, and then dried in a warm oven (60 °C). The yield was 3.3566 g (35.2%). Anal. Calc. for \(\text{C}_{32}\text{H}_{62}\text{NiO}_4\) (FW, 569.53 g mol\(^{-1}\)): C, 67.4; H, 10.9 Found: C, 66.9; H, 11.0%.

(d) \([\text{Co(C}_3\text{H}_3(\text{CH}_2)_{14}\text{COO})_2]\)

CoCl\(_2\cdot6\text{H}_2\text{O}\) (2.18 g; 16.79 mmol) was added to a hot solution of \(\text{CH}_3(\text{CH}_2)_{14}\text{COONa}\) (5.12 g; 18.3 mmol) in ethanol (100 mL). The mixture was then heated for another 30 minutes. A fine purple powder formed was filtered under suction, washed with distilled water followed by ethanol, and then dried in a warm oven (60 °C). The yield was 4.48 g (46.8%). Anal. Calc. \(\text{C}_{32}\text{H}_{62}\text{CoO}_4\) for (FW, 569.76 g mol\(^{-1}\)): C, 67.5; H, 11.0 Found: C, 68.0; H, 10.8%.

(e) \([\text{Fe(C}_3\text{H}_3(\text{CH}_2)_{14}\text{COO})_2(\text{CH}_3\text{CH}_2\text{OH})]\)

FeSO\(_4\cdot7\text{H}_2\text{O}\) (5.10 g; 18.3 mmol) was added to a hot solution of \(\text{CH}_3(\text{CH}_2)_{14}\text{COONa}\) (10.23 g; 36.7 mmol) in \(\text{CH}_3\text{CH}_2\text{OH}\) (100 mL). The mixture was then heated for another 30 minutes. A fine light brown powder formed was filtered under suction, washed with distilled water followed by ethanol, and then dried in a warm oven (60 °C). The yield was 8.26 g (73.7%). Anal. Calc. for \(\text{C}_{34}\text{H}_{68}\text{FeO}_5\) (FW, 612.75 g mol\(^{-1}\)): C, 66.6; H, 11.2 Found: C, 66.4 ; H, 12.5%.

3.3.3 Reaction of \(\text{H}_2\text{L}1\) with \([\text{M(CH}_3(\text{CH}_2)_{14}\text{COO})_2]\)

(a) \([\text{Cu(C}_3\text{H}_3(\text{CH}_2)_{14}\text{COO})_2]\)

\([\text{Cu(C}_3\text{H}_3(\text{CH}_2)_{14}\text{COO})_2]\) (0.57 g; 1.0 mmol) was dissolved in ethanol (100 mL). The mixture was gently heated and stirred. \(\text{H}_2\text{L}1\) (0.352 g; 1.0 mmol) was slowly added to
the mixture and the reflux continued for 3 hours. The colour of the solution changed from clear yellowish to dark brown. The solution was then left for two days at room temperature, and the solid formed was filtered. The yield was 0.38 g (92%). Anal. Calc. for C_{22}H_{26}CuN_{2}O_{2} (FW, 414 g mol\(^{-1}\)): C, 63.8; H, 6.3; N, 6.7. Found: C, 63.2; H, 6.5; N, 6.8%.

(b) \([\text{Ni}(CH_3(CH_2)_{14}COO)]_2\]

[Ni(CH_3(CH_2)_{14}COO)]_2 (0.28 g; 0.49 mmol) and H_2L1 (0.35 g; 1.0 mmol) was reacted in the same manner as in 3.3.3(a). The colour of the solution changed from light green to dark green. The solution was then left for two days to let the product precipitate out. The filtered residue was then dried at room temperature. The yield was 0.19 g (39.7%). Anal. Calc. for C_{22}H_{26}NiN_{2}O_{2} (FW, 409 g mol\(^{-1}\)): C, 64.6; H, 6.4; N, 6.9. Found: C, 64.8; H, 6.7; N, 6.8%.

(c) \([\text{Co}(CH_3(CH_2)_{14}COO)]_2\]

The same procedure was the same as in 3.3.3(a), replacing [Cu(CH_3(CH_2)_{14}COO)]_2 with [Co(CH_3(CH_2)_{14}COO)]_2 (0.57 g; 1.0 mmol). The colour changes of the solution was observed from light green to dark green. The precipitates from the reaction was filtered and dried at room temperature. The yield was 0.32 g (78.7%). Anal. Calc. for C_{22}H_{26}CoN_{2}O_{2} (FW, 409.39 g mol\(^{-1}\)): C, 64.5; H, 6.4; N, 6.8. Found: C, 65.1; H, 6.5; N, 6.9%.

(d) \([\text{Fe}(CH_3(CH_2)_{14}COO)]_2\]

[Fe(CH_3(CH_2)_{14}COO)]_2(CH_3CH_2OH)] (0.42 g; 0.69 mmol) and H_2L1 (0.27 g; 0.76 mmol) was reacted same as in 3.3.3(a). The colour of the solution changed from clear yellowish to light brown. The brown solid formed was filtered and dried at room
temperature. The yield was 0.35 g (46.6%). *Anal.* Calc. C_{54}H_{102}Fe_{2}N_{2}O_{13} for (FW, 1090.61 g mol^{-1}): C, 59.5; H, 9.2; N, 2.5 Found: C, 59.1; H, 8.6; N, 2.9%.

### 3.3.4 Reaction of H2L2 with [M(CH3(CH2)14COO)2]

(a) Step-wise reaction

(i) [Cu(CH3(CH2)14COO)2]

H2L2 (0.38 g; 1.0 mmol) was dissolved in ethanol (100 mL). The solution was magnetically stirred and heated for about 10 minutes. A suspension of [Cu(CH3(CH2)14COO)2] (0.57 g; 1.0 mmol) in ethanol was slowly added to the yellow solution. The mixture colour turn green and left to be refluxed for 3 hours. After 3 hours of refluxed, the mixture was then left for a few days to let the product precipitate out. The yield was 0.30 g (67.9%). *Anal.* Calc. for C_{48}H_{60}Cu_{2}N_{4}O_{13} (FW: 442.05 g mol^{-1}): C, 65.2; H, 6.8; N, 6.3 Found: C, 65.9; H, 7.0; N, 6.2%.

(ii) [Ni(CH3(CH2)14COO)(H2O)2]

The procedure was the same as in 3.3.4(a)(i), replacing [Cu(CH3(CH2)14COO)2] with [Ni(CH3(CH2)14COO)2] (0.56 g; 0.1 mmol). The colour of the solution changed from light green to dark green. The solution was then left overnight before being filtered. Both the residue and the filtrate were kept. The yield was 0.33 g (68.3%). *Anal.* Calc. for C_{26}H_{36}N_{2}NiO_{3} (FW: 483.2 g mol^{-1}): C, 64.6; H, 7.5; N, 5.8. Found: C, 65.0; H, 7.7; N, 5.5%.

(iii) [Co(CH3(CH2)14COO)2]

The procedure was the same as in 3.3.4(a)(i), replacing [Cu(CH3(CH2)14COO)2] with [Co(CH3(CH2)14COO)2] (0.57 g; 1.0 mmol). The colour of the solution changed from light green to dark green. The solution was then left for 2 days at room temperature. The dark green solid residue was filtered. The yield was 0.36 g (25.0%). *Anal.* Calc. for
C₈₀H₁₁₆Co₂N₆O₁₀ (FW: 1438.74 g mol⁻¹): C, 66.8; H, 8.1; N, 5.8. Found: C, 66.8; H, 7.6; N, 5.8%.

(iv) [Fe(CH₃(CH₂)₄COO)₂CH₃CH₂OH]
The procedure was the same as in 3.3.4(a)(i), replacing [Cu(CH₃(CH₂)₁₄COO)₂] [Fe(CH₃(CH₂)₁₄COO)₂(CH₃CH₂OH)] (0.28 g; 0.46 mmol). The colour of the solution changed from clear yellowish to dark brown. The black gummy solid formed was filtered and left standing at room temperature. The yield was 0.29 g (40.4%). Anal. Calc. for C₈₈H₁₂₉Fe₂N₆O₁₁ (FW: 1558.69 g mol⁻¹): C, 67.8; H, 8.3; N, 5.4 Found: C, 66.8; H, 7.6; N, 5.5%.

(b) One-pot reaction
(i) [Cu(L2)]
1,10-diaminoctane (0.43 g; 2.50 mmol) was dissolved in about 100 mL of ethanol. The clear solution was slowly heated and stirred for about 10 minutes. Then 2-hydroxybenzaldehyde (0.61 g; 5.0 mmol) was slowly added to the hot solution. [Cu(CH₃(CH₂)₁₄COO)₂] (0.90 g; 1.57 mmol) was added to the mixture. A few drops of glacial acetic acid was added as catalyst. The mixture was then refluxed for 3 hours. The precipitate formed was filtered. The yield was 0.63 g (90.1%). Anal. Calc. for C₂₄H₃₀CuN₂O₂ (FW: 442.06 g mol⁻¹): C, 65.2; H, 6.8; N, 6.3 Found: C, 66.5; H, 7.1; N, 6.3%.

(ii) [Ni₂(L2)(HL₂)₂].H₂O
1,10-diaminoctane (3.44 g; 20.0 mmol), 2-hydroxybenzaldehyde (4.88 g; 40.0 mmol) and [Ni(CH₃(CH₂)₁₄COO)₂] (1.50 g; 2.63 mmol) was reacted together as in 3.3.4(b)(i). The precipitate formed was filtered and analysed. The yield was 1.01 g (87.8%). Anal. Calc. for C₇₂H₇₄N₆Ni₂O₇ (FW: 1272.9 g mol⁻¹): C, 67.9; H, 7.4; N, 6.4 Found: C, 67.2; H, 7.1; N, 6.4%.
(iii) [Co(L2)(HL2)]

1,10-diaminooctane (0.86 g; 5.0 mmol), 2-hydroxybenzaldehyde (1.22 g; 10.0 mmol) and [Co(CH₃(CH₂)₁₄COO)₂] (1.42 g; 2.5 mmol) was reacted together using the same procedure as in 3.3.4(b)(i). The black solution was left to cool to let the product precipitated out. The yield was 0.67 g (32.8%). Anal. Calc. for C₄₈H₆₁CoN₄O₄ (FW: 816.96 g mol⁻¹): C, 70.6; H, 7.5; N, 6.8 Found: C, 70.1; H, 7.6; N, 6.7%.

(iv) [Fe⁺ⅡFe⁺Ⅲ(CH₃(CH₂)₁₄COO)(L2)(HL2)₂(EtOH)₂].2EtOH

The procedure was the same as in 3.3.4(b)(iii), replacing [Co(CH₃(CH₂)₁₄COO)₂] with [Fe(CH₃(CH₂)₁₄COO)₂(CH₃CH₂OH)] (1.43 g; 2.3 mmol). The black solution was left to cool to let the product precipitated out. The yield was 1.95 g (50.7%). Anal. Calc. for C₉₆H₁₄₇Fe₂N₆O₁₁ (FW: 1672.92 g mol⁻¹): C, 68.2; H, 8.8; N, 4.9 Found: C, 68.0; H, 8.6; N, 4.7%.

3.3.5 Reaction of H₂L₃ with [M(CH₃(CH₂)₁₄COO)₂]

(a) [Cu(CH₃(CH₂)₁₄COO)₂]

H₂L₃ (0.12 g; 0.39 mmol) was dissolved in ethanol (100 mL). The solution was magnetically stirred and heated for about 10 minutes. A suspension of [Cu(CH₃(CH₂)₁₄COO)₂] (0.23 g; 0.4 mmol) in ethanol was slowly added to the yellow solution. The mixture colour turn green and left to be refluxed for 3 hours. After 3 hours of refluxed, the mixture was then left for a few days to let the product precipitate out. The yield was 0.13 g (64.8%). Anal. Calc. for C₅₄H₇₂Cu₂N₄O₆ (FW: 1001.3 g mol⁻¹): C, 64.7; H, 7.4; N, 5.6. Found: C, 64.5; H, 7.5; N, 5.8%.
(b) \([\text{Ni(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\)

The procedure was the same as in 3.3.5(a), replacing \([\text{Cu(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\) with \([\text{Ni(CH}_3\text{(CH}_2)_{14}\text{COO)}\text{Cl(H}_2\text{O)}_2]\\) (0.15 g; 2.6 mmol). The colour of the solution changed from light yellow to light green. The solution was then left for 2 days before being filtered. Both the residue and the filtrate are kept. The yield was 0.19 g (77.2%). *Anal.* Calc. for \(\text{C}_{54}\text{H}_{75}\text{NiN}_4\text{O}_6\) (FW: 934.89 g mol\(^{-1}\)): C, 70.2; H, 8.4; N, 5.9. Found: C, 69.5; H, 8.1; N, 5.9%.

(c) \([\text{Co(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\)

The procedure was the same as in 3.3.5(a), replacing \([\text{Cu(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\) with \([\text{Co(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\) (0.11 g; 0.2 mmol) and \(\text{H}_2\text{L}_3\\) (0.06 g; 0.2 mmol). The colour of the solution changed from light green to dark green. The solution was then left for 2 days at room temperature. The dark green solid residue was filtered. The filtrate was kept for further viewing. The yield was 0.11 g (80.3%). *Anal.* Calc. for \(\text{C}_{35}\text{H}_{51}\text{CoN}_2\text{O}_4\\) (FW: 623.7 g mol\(^{-1}\)): C, 67.5; H, 9.9; N, 4.5. Found: C, 67.5; H, 8.3; N, 4.5%.

(d) \([\text{Fe(CH}_3\text{(CH}_2)_{14}\text{COO)}_2(\text{CH}_3\text{CH}_2\text{OH})]\\)

The procedure was the same as in 3.3.5(a), replacing \([\text{Cu(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\) with \([\text{Fe(CH}_3\text{(CH}_2)_{14}\text{COO)}_2]\\). \(\text{CH}_3\text{CH}_2\text{OH}\\) (0.4289 g; 0.70 mmol) and \(\text{H}_2\text{L}_3\\) (0.22 g; 0.71 mmol). The colour of the solution changed from clear yellowish to dark brown. The black gummy solid formed was filtered and left standing at room temperature. The yield was 0.1170 g (19.1%). *Anal.* Calc. for \(\text{C}_{51}\text{H}_{85}\text{FeN}_2\text{O}_2\\) (FW: 876.06 g mol\(^{-1}\)): C, 69.9; H, 9.55; N, 3.2. Found: C, 70.0; H, 10.3; N, 4.3%.
3.4 Instrumental Analyses

3.4.1 Elemental analyses
The percentages of carbon, hydrogen and nitrogen in a compound were determined on a Perkin Elmer CHNS/O analyser 2400 Series II. A small amount of the sample (1-2 mg) was placed in a tin capsule of dimension 5 mm x 8 mm, which was then folded into a tiny piece. It was then put into the analyser and heated up to 1000 ºC.

3.4.2 $^1$H-Nuclear magnetic resonance spectroscopy
The $^1$H-nuclear magnetic resonance spectra ($^1$H-NMR) were recorded on a JEOL FT-NMR Lambda 400 MHz spectrometer. A small amount of the sample was dissolved in a suitable deuterated solvent and placed inside an NMR tube.

3.4.3 Fourier transform infrared spectroscopy
The IR spectrum were recorded using a Perkin-Elmer Spectrum 400 FT-IR/FT-IR Spectrometer with a Pike Technologies GladiATR attachment.

3.4.4 Ultraviolet-visible spectroscopy
The ultraviolet spectra were recorded from 1000 – 300 nm with Shimadzu UV-vis-NIR 3600 spectrophotometer for both liquid and solid samples.
For solution, an exactly known mass of the solid was dissolved in a suitable solvent in a volumetric flask. Then part of the solution was placed into a 1cm quartz cuvette which is later put into the sample holder. The spectrum was recorded with the corresponding solvent as reference.
3.4.5 Differential scanning calorimetry

All the thermograms were obtained for differential scanning calorimetry (DSC) from a Perkin Elmer DSC 6 calorimeter within the temperature range of 35 – 300 °C and scan rate of 10 °C min\(^{-1}\).

Mass of the sample (2 – 4 mg) was recorded using the microbalance before it was transferred into an aluminium crucible and placed inside the instrument. The analysis was performed under nitrogen gas with a flow rate of 10 cm\(^3\) min\(^{-1}\).

3.4.6 Thermogravimetry

Thermogram of all complexes were recorded using a Pyris Diamond TG/DTA Perkin Elmer instrument with temperature range of 50 – 900 °C with scan rate of 20 °C min\(^{-1}\). The analysis was done under nitrogen with a flow rate of 10 cm\(^3\) min\(^{-1}\). An alumina pan was used as a sample holder. The sample (4 – 5 mg) was placed inside the pan and the instrument.

3.4.7 Room temperature magnetic susceptibility

The magnetic susceptibility was recorded using a Sherwood Auto Magnetic Susceptibility Balance. An empty glass tube was tared on an analytical balance before placing it on the instrument. The exponent of the reading was changed to 10\(^{-5}\) and tared again. Sample preparation started with the sample being ground finely and packed into the tube up to the optimum mark (4 cm in length) and the mass was recorded. The tube was then placed in the instrument before the weight and height of the sample was keyed in. The \(\chi_\ell\) was recorded.
3.4.8 Variable temperature magnetic susceptibility

The measurement was done using a Quantum Design Magnetic Property Measurement System (MPMS) – XL EverCool superconducting quantum interference device (SQUID) magnetometer in Kinki University, Higashiosaka-shi, Osaka, Japan. About 10 mg of the sample was put inside a medicine capsule and insert halfway inside a straw which is roughly 10 centimeter from the top. The straw was then put inside the instrument to be analysed. The measurements were done at 1 Tesla or 10000 Gauss and the temperature range is 300 – 2 Kelvin. The raw data from the measurement was then further analysed using Microsoft Excel and Igor Software.

3.4.9 Polarized Optical Microscopy

Mesomorphism of samples were recorded with Olympus BX51 polarizing microscope equipped with a Mettler Toledo FP90 method controller and FP82HT hot stage. A tiny amount of the samples were sandwiched between two thin glass slides and placed on the hot stage. Then the samples were heated and cooled at various rate ranging from 1 – 10 °C min⁻¹.

References
