CHAPTER 3 EXPERIMENTAL

3.1 Introduction

This research is focused on the synthesis and characterization of complexes of Cu(II) ($d^9$), Ni(II) ($d^8$), Co(II) ($d^7$) and Fe(II) ($d^6$) ions with mixed ligands (ethanoate or hexadecanoate, and conjugated imine or amide). These complexes were designed to be low band-gap solar cell and/or spin crossover materials, and for the hexadecanoate complexes, mesogenic materials.

The imine and amide ligands were synthesized from the condensation reaction of 2,4-diamino-6-phenyl-1,3,5-triazine with: (a) pyrrole-2-carboxaldehyde to form $H_2L_1$; (b) 2,5-thiophenedicarboxaldehyde to form $L_2$; (c) 2,5-thiophenedicarboxylic acid to form $L_3$; and (d) acetylenedicarboxylic acid to form $L_4$. These ligands were then reacted with [M(RCOO)$_2$] (M = Cu, Ni, Co, Fe; R = CH$_3$COO and CH$_3$(CH$_2$)$_{14}$COO). The general synthetic paths for these ligands and complexes are shown in Scheme 3.1.

Scheme 3.1 General synthetic paths for Complexes 1-32

A total of four ligands, 8 precursor complexes and 32 designed complexes were synthesized and characterized. The ligands were characterized by $^1$H-nuclear magnetic
resonance spectroscopy (\(^1\)H-NMR), CHN elemental analyses, and FTIR spectroscopy. The complexes were characterized by CHN elemental analyses, FTIR spectroscopy, UV-vis spectroscopy, fluorescence spectroscopy, magnetic susceptibility by the Guoy method, thermogravimetry (TGA), differential scanning calorimetry (DSC), polarised optical microscopy (POM), and cyclic voltammetry (CV).

### 3.2 Chemicals

All chemicals (Table 3.1) were commercially available and used as received.

**Table 3.1** Chemicals used in the research, arranged in alphabetical order

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Formula Weight (g mol(^{-1}))</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylenedicarboxylic acid</td>
<td>HOOC-C≡C-COOH</td>
<td>114.06</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Cobalt(II) acetate tetrahydrate</td>
<td>Co( CH(_3)COO)(_2).4(H_2)O</td>
<td>249.08</td>
<td>R&amp;M</td>
</tr>
<tr>
<td>Cobalt(II) chloride hexahydrate</td>
<td>CoCl(_2).6(H_2)O</td>
<td>237.93</td>
<td>R&amp;M</td>
</tr>
<tr>
<td>Copper(II) acetate</td>
<td>Cu(CH(_3)COO)(_2)</td>
<td>181.63</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Copper(II) chloride dihydrate</td>
<td>CuCl(_2).2(H_2)O</td>
<td>170.48</td>
<td>R&amp;M</td>
</tr>
<tr>
<td>2,4-Diamino-6-phenyl-1,3,5-triazine</td>
<td>C(_9)H(_9)N(_5)</td>
<td>187.20</td>
<td>Merck</td>
</tr>
<tr>
<td>Iron(II) acetate</td>
<td>Fe(CH(_3)COO)(_2)</td>
<td>173.93</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Iron(II) chloride tetrahydrate</td>
<td>FeCl(_2).4(H_2)O</td>
<td>198.81</td>
<td>R&amp;M</td>
</tr>
<tr>
<td>Nickel(II) acetate tetrahydrate</td>
<td>Ni(CH(_3)COO)(_2).4(H_2)O</td>
<td>248.84</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Nickel(II) chloride hexahydrate</td>
<td>NiCl(_2).6(H_2)O</td>
<td>237.69</td>
<td>R&amp;M</td>
</tr>
<tr>
<td>hexadecanoic acid</td>
<td>CH(_3)(CH(<em>2))(</em>{14})COOH</td>
<td>256.42</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Pyrrole-2-carboxaldehyde</td>
<td>C(_5)H(_5)NO</td>
<td>95.10</td>
<td>Merck</td>
</tr>
<tr>
<td>2,5-Thiophenedicarboxaldehyde</td>
<td>C(_6)H(_4)O(_2)S</td>
<td>241.46</td>
<td>Aldrich</td>
</tr>
<tr>
<td>2,5-Thiophenedicarboxylic acid</td>
<td>C(_6)H(_4)O(_2)S</td>
<td>172.16</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
3.3 Syntheses

3.3.1 Ligands

(a) $H_2L1$, $C_{19}H_{15}N_7$

An ethanolic solution of pyrrole-2-carboxaldehyde (11.69 g; 123 mmol) was added into an ethanolic suspension of 2,4-diamino-6-phenyl-1,3,5-triazine (11.52 g; 61.5 mmol), followed by a few drops of glacial acetic acid. The reaction mixture was heated under reflux for 2 hours. A brownish precipitate formed was filtered off from the hot reaction mixture, and washed with ethanol, and dried in an oven at 80°C. The yield was 15.84 g (68.3%).

(b) $L2$, $C_{19}H_{21}N_5O_2S$

The procedure was the same as for $H_2L1$ (Section 3.3.1(a)), using 2,4-diamino-6-phenyl-1,3,5-triazine (2.83 g; 15.1 mmol) and 2,5-thiophenedicarboxaldehyde (3.64 g; 15.1 mmol). The product was a brown powder, and the yield was 5.74 g (88.7%).

(c) $L3$, $C_{15}H_{11}N_5O_3S$

2,4-Diamino-6-phenyl-1,3,5-triazine (18.89 g; 100.9 mmol) was added portionwise to a solution of 2,5-thiophenedicarboxylic acid (12.93 g; 100.9 mmol) in absolute ethanol (100 mL). The mixture was refluxed for 2 hours and then left to cool to room temperature. A white powder formed was filtered off, washed with ethanol and dried in an oven at 80°C. The yield was 31.15 g (97.9%).

(d) $L4$, $C_{13}H_7N_5O_2$

The procedure was the same as for $L3$ (Section 3.3.1(c)), using 2,4-diamino-6-phenyl-1,3,5-triazine (6.38 g; 34.0 mmol) and acetylenedicarboxylic acid (3.88 g; 34.0 mmol). The product was a pale yellow powder, and the yield was 8.04 g (78.4%).
3.3.2 Metal(II) hexadecanoates

(a) Copper(II) hexadecanoate

A suspension of hexadecanoic acid (33.59 g; 130.9 mmol) in aqueous ethanol (v/v, 1:1; 200 mL) was magnetically stirred and heated on a hot plate until a clear solution formed (about 2 hours). A solution of sodium carbonate (6.94 g; 65.5 mmol) was then added portionwise, and the reaction mixture was magnetically stirred and heated for another hour. The solvents were removed on a rotary evaporator to give sodium hexadecanoate as a white powder. The yield was 36.51 g (90.1%).

Sodium hexadecanoate (7.03 g; 25.3 mmol) was dissolved in aqueous ethanol (v/v, 1:1; 200 mL). Copper(II) chloride dihydrate (2.15 g; 12.5 mmol) was added gradually to the solution, the mixture was stirred and heated for 30 minutes, and left to cool to room temperature. The greenish-blue precipitate formed was filtered off, washed with ethanol and dried in an oven at 80°C. The yield was 6.53 g (71.1%).

(b) Nickel(II) hexadecanoate

The procedure was the same as for copper(II) hexadecanoate (Section 3.3.2(a)), using sodium hexadecanoate (7.63 g; 27.0 mmol) and nickel(II) chloride hexahydrate (3.26 g; 13.5 mmol). The product was a greenish powder, and the yield was 7.77 g (71.3%).

(c) Cobalt(II) hexadecanoate

The procedure was the same as for copper(II) hexadecanoate (Section 3.3.2(a)), using sodium hexadecanoate (7.05 g; 25.3 mmol) and cobalt(II) chloride hexahydrate (3.01 g; 12.5 mmol). The product was a purple powder, and the yield was 7.13 g (70.9%).

(d) Iron(II) hexadecanoate

The procedure was the same as for copper(II) hexadecanoate (Section 3.3.2(a)), using sodium hexadecanoate (7.70 g; 27.9 mmol) and iron(II) chloride tetrahydrate (2.75 g; 13.8 mmol). The product was a brown powder, and the yield was 7.57 g (72.4%).
3.3.3 Metal(II) carboxylate-L1 complexes

(a) \([\text{Cu}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2(L1)]\) (Complex 1)

Copper(II) ethanoate (0.91 g; 5.0 mmol) was added to an ethanolic suspension of C\(_{19}\)H\(_{15}\)N\(_7\) (1.71 g; 5.0 mmol), and the mixture was heated under reflux for 3 hours. The green powder formed was filtered from the hot reaction mixture, washed with ethanol, was dried in an oven at 100°C. The yield was 2.29 g (87.4%).

(b) \([\text{Ni}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2(L1)]\) (Complex 2)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using nickel(II) ethanoate tetrahydrate (2.38 g; 9.6 mmol) and C\(_{19}\)H\(_{15}\)N\(_7\) (3.26 g; 9.6 mmol). The product was a grey powder, and the yield was 4.77 g (84.6%).

(c) \([\text{Co}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2(L1)]\) (Complex 3)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using cobalt(II) ethanoate tetrahydrate (1.46 g; 5.9 mmol) and C\(_{19}\)H\(_{15}\)N\(_7\) (2.0 g; 5.9 mmol). The product was a purple powder, and the yield was 4.13 g (92.6%).

(d) \([\text{Fe}_3(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_3(L1)].\text{H}_2\text{O}\) (Complex 4)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using iron(II) ethanoate (0.96 g; 5.5 mmol), C\(_{19}\)H\(_{15}\)N\(_7\) (1.89 g; 5.5 mmol), and about 0.1 g of ascorbic acid (as an antioxidant). The product was a black solid, and the yield was 2.77 g (97.2%).

(e) \([\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(L1)]\) (Complex 5)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using copper(II) hexadecanoate (2.29 g; 2.0 mmol) and C\(_{19}\)H\(_{15}\)N\(_7\) (0.68 g; 2.0 mmol). The product was a green powder, and the yield was 2.23 g (75.0%).
(f) $[\text{Ni}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(\text{H}_2\text{O})_2(\text{L1})] \ (\text{Complex } 6)$

The procedure was the same as for copper(II) ethanoate-$\text{L1}$ (Section 3.3.3(a)), using nickel(II) hexadecanoate (0.09 g; 0.2 mmol) and $\text{C}_{19}\text{H}_{15}\text{N}_7$ (0.05 g; 0.2 mmol). The product was a greenish powder, and the yield was 0.13 g (92.8%).

(g) $[\text{Co}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(\text{H}_2\text{O})_2(\text{L1})] \ (\text{Complex } 7)$

The procedure was the same as for copper(II) ethanoate-$\text{L1}$ (Section 3.3.3(a)), using cobalt(II) hexadecanoate (0.15 g; 0.3 mmol) and $\text{C}_{19}\text{H}_{15}\text{N}_7$ (0.09 g; 0.3 mmol). The product was a blue powder, and the yield was 0.18 g (75.0%).

(h) $[\text{Fe}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(\text{H}_2\text{O})_2(\text{L1})] \ (\text{Complex } 8)$

The procedure was the same as for copper(II) ethanoate-$\text{L1}$ (Section 3.3.3(a)), using iron(II) hexadecanoate (0.15 g; 0.3 mmol), $\text{C}_{19}\text{H}_{15}\text{N}_7$ (0.09 g; 0.3 mmol), and about 0.1 g of ascorbic acid. The product was a cream powder, and the yield was 0.21 g (87.5%).

3.3.4 Metal(II) carboxylate-$\text{L}_2$ complexes

(a) $[[\text{Cu}(\text{CH}_3\text{COO})_2(\text{L}_2)].\text{H}_2\text{O}]_n \ (\text{Complex } 9)$

The procedure was the same as for copper(II) ethanoate-$\text{L1}$ (Section 3.3.3(a)), using copper(II) ethanoate (0.13 g; 0.7 mmol) and $\text{C}_{19}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ (0.34 g; 0.7 mmol). The product was a green powder, and the yield was 0.33 g (70.2%).

(b) $[[\text{Ni}(\text{CH}_3\text{COO})(\text{L}_2)].2\text{H}_2\text{O}]_n \ (\text{Complex } 10)$

The procedure was the same as for copper(II) ethanoate-$\text{L1}$ (Section 3.3.3(a)), using nickel(II) ethanoate tetrahydrate (0.35 g; 1.4 mmol) and $\text{C}_{19}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ (0.45 g; 1.4 mmol). The product was a pale green powder, and the yield was 0.63 g (78.8%).
(c) \[[Co(CH_3COO)z(L2)].2H_2O\]_n (Complex 11)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using cobalt(II) ethanoate tetrahydrate (0.18 g; 0.7 mmol) and C_{19}H_{21}N_5O_2S (0.25 g; 0.7 mmol). The product was a purple powder, and the yield was 0.35 g (81.4%).

(d) \[[Fe(CH_3COO)z(L2)].2H_2O\]_n (Complex 12)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using iron(II) ethanoate (0.18 g; 1.0 mmol), C_{19}H_{21}N_5O_2S (0.34 g; 1.0 mmol), and about 0.1 g ascorbic acid. The product was a brown powder, and the yield was 0.43 g (82.7%).

(e) \[[Cu(CH_3(CH_2)_14COO)z(L2)].H_2O\]_n (Complex 13)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using copper(II) hexadecanoate (1.17 g; 1.0 mmol) and C_{19}H_{21}N_5O_2S (0.49 g; 1.0 mmol). The product was a green powder, and the yield was 1.41 g (85.5%).

(f) \[[Ni(CH_3(CH_2)_14COO)z(L2)].2H_2O\]_n (Complex 14)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using nickel(II) hexadecanoate (0.75 g; 1.3 mmol) and C_{19}H_{21}N_5O_2S (0.63 g; 1.3 mmol). The product was a yellow-green powder, and the yield was 0.92 g (66.7%).

(g) \[[Co(CH_3(CH_2)_14COO)z(L2)].2H_2O\]_n (Complex 15)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using cobalt(II) hexadecanoate (0.62 g; 1.1 mmol) and C_{19}H_{21}N_5O_2S (0.53 g; 1.1 mmol). The product was a pale purple powder, and the yield was 0.95 g (82.6%).

(h) \[[Fe(CH_3(CH_2)_14COO)z(L2)].2H_2O\]_n (Complex 16)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using iron(II) hexadecanoate (0.94 g; 1.7 mmol), C_{19}H_{21}N_5O_2S (0.79 g; 1.7 mmol), and about
0.1 g ascorbic acid. The product was an orange powder, and the yield was 1.08 g (62.6%).

### 3.3.5 Metal(II) carboxylate-L3 complexes

(a) \([[\text{Cu(CH}_3\text{COO})_2(L3)]]_n\) (Complex 17)

The procedure was the same as for copper(II) ethanoate-\(L1\) (Section 3.3.3(a)), using copper(II) ethanoate (1.42 g; 7.0 mmol) and \(\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (2.39 g; 7.0 mmol). The product was a green powder, and the yield was 2.57 g (67.5%).

(b) \([[\text{Ni}_2(\text{CH}_3\text{COO})_4(L3)]\cdot5\text{H}_2\text{O}]]_n\) (Complex 18)

The procedure was the same as for copper(II) ethanoate-\(L1\) (Section 3.3.3(a)), using nickel(II) ethanoate tetrahydrate (1.95 g; 7.8 mmol) and \(\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (2.66 g; 7.8 mmol). The product was a green powder, and the yield was 3.58 g (77.7%).

(c) \([[\text{Co(CH}_3\text{COO})_2(L3)]\cdot2\text{H}_2\text{O}]]_n\) (Complex 19)

The procedure was the same as for copper(II) ethanoate-\(L1\) (Section 3.3.3(a)), using cobalt(II) ethanoate tetrahydrate (1.97 g; 7.9 mmol) and \(\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (2.69 g; 7.9 mmol). The product was a purple powder, and the yield was 3.64 g (78.1%).

(d) \([[\text{Fe}_2(\text{CH}_3\text{COO})_4(L3)]\cdot2\text{H}_2\text{O}]]_n\) (Complex 20)

The procedure was the same as for copper(II) ethanoate-\(L1\) (Section 3.3.3(a)), using iron(II) ethanoate (1.92 g; 11 mmol), \(\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (3.75 g; 11 mmol), and about 0.1 g ascorbic acid. The product was a brown powder, and the yield was 4.98 g (87.8%).

(e) \([[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_4\text{COO})_4(L3)]\cdot2\text{H}_2\text{O}]]_n\) (Complex 21)

The procedure was the same as for copper(II) ethanoate-\(L1\) (Section 3.3.3(a)), using copper(II) hexadecanoate (0.54 g; 0.5 mmol) and \(\text{C}_{15}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (0.16 g; 0.5 mmol). The product was a pale yellow powder, and the yield was 0.53 g (75.7%).
(f) \([\text{Ni}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_4(L_3)]_n\) (Complex 22)

The procedure was the same as for copper(II) ethanoate-\(L_1\) (Section 3.3.3(a)), using nickel(II) hexadecanoate (0.80 g; 1.4 mmol) and \(\text{C}_{13}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (0.48 g; 1.4 mmol). The product was a pale greenish powder, and the yield was 0.84 g (65.6%).

(g) \([\text{Co}(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(L_3)]_n\) (Complex 23)

The procedure was the same as for copper(II) ethanoate-\(L_1\) (Section 3.3.3(a)), using cobalt(II) hexadecanoate (0.24 g; 0.4 mmol) and \(\text{C}_{13}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (0.14 g; 0.4 mmol). The product was a blue powder, and the yield was 0.24 g (64.9%).

(h) \([\text{Fe}(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(L_3)].3\text{H}_2\text{O}]_n\) (Complex 24)

The procedure was the same as for copper(II) ethanoate-\(L_1\) (Section 3.3.3(a)), using iron(II) hexadecanoate (0.33 g; 0.6 mmol), \(\text{C}_{13}\text{H}_{11}\text{N}_5\text{O}_3\text{S}\) (0.19 g; 0.6 mmol), and about 0.1 g ascorbic acid. The product was a pink powder, and the yield was 0.38 g (73.0%).

3.3.6 Metal(II) carboxylates-\(L_4\) complexes

(a) \([\text{Cu}(\text{CH}_3\text{COO})_2(L_4)]_n\) (Complex 25)

The procedure was the same as for copper(II) ethanoate-\(L_1\) (Section 3.3.3(a)), using copper(II) ethanoate (0.51 g; 2.8 mmol) and \(\text{C}_{13}\text{H}_7\text{N}_5\text{O}_2\) (0.74 g; 2.8 mmol). The product was a green powder, and the yield was 1.23 g (98.4%).

(b) \([\text{Ni}_2(\text{CH}_3\text{COO})_4(L_4)]_n\) (Complex 26)

The procedure was the same as for copper(II) ethanoate-\(L_1\) (Section 3.3.3(a)), using nickel(II) ethanoate tetrahydrate (0.58 g; 2.3 mmol) and \(\text{C}_{13}\text{H}_7\text{N}_5\text{O}_2\) (0.66 g; 2.3 mmol). The product was a pale green powder, and the yield was 1.13 g (91.1%).
(c) \([\text{Co}(\text{CH}_3\text{COO})_2(L4)].2\text{H}_2\text{O}]_n\) (Complex 27)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using cobalt(II) ethanoate tetrahydrate (0.66 g; 2.7 mmol) and C_{13}H_{7}N_{5}O_{2} (0.71 g; 2.7 mmol). The product was a purple powder, and the yield was 1.17 g (85.4%).

(d) \([\text{Fe}_2(\text{CH}_3\text{COO})_4(L4)].2\text{H}_2\text{O}]_n\) (Complex 28)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using iron(II) ethanoate (0.56 g; 3.2 mmol), C_{13}H_{7}N_{5}O_{2} (0.85 g; 3.2 mmol), and about 0.1 g ascorbic acid. The product was a brown powder, and the yield was 1.12 g (79.4%).

(e) \([\text{Cu}(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(L4)]_n\) (Complex 29)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using copper(II) hexadecanoate (0.34 g; 0.3 mmol) and C_{13}H_{7}N_{5}O_{2} (0.08 g; 0.3 mmol). The product was a green powder, and the yield was 0.37 g (89.2%).

(f) \([\text{Ni}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_4(L4)]_n\) (Complex 30)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using nickel(II) hexadecanoate (0.47 g; 0.8 mmol) and C_{13}H_{7}N_{5}O_{2} (0.24 g; 0.8 mmol). The product was a pale green powder, and the yield was 0.43 g (60.6%).

(g) \([\text{Co}(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(L4)].2\text{H}_2\text{O}]_n\) (Complex 31)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using cobalt(II) hexadecanoate (0.22 g; 0.4 mmol) and C_{13}H_{7}N_{5}O_{2} (0.11 g; 0.4 mmol). The product was a bluish-green powder, and the yield was 0.20 g (60.7%).

(h) \([\text{Fe}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_4(L4)].2\text{H}_2\text{O}]_n\) (Complex 32)

The procedure was the same as for copper(II) ethanoate-L1 (Section 3.3.3(a)), using iron(II) hexadecanoate (0.79 g; 1.4 mmol), C_{13}H_{7}N_{5}O_{2} (0.39 g; 1.4 mmol), and about
0.1 g ascorbic acid. The final product was a grey powder, and the yield was 0.72 g (61.0%).

3.4 Instrumental Analyses
3.4.1 Elemental analyses
The elemental analyses were recorded on a Perkin-Elmer CHNO/S 2400 Series II elemental analyser. The sample (about 1-2 mg) was wrapped in a thin aluminium capsule (5 x 8 mm) and folded into a tiny piece. It was then placed into the analyzer and heated to a maximum temperature of 1000 ºC.

3.4.2 Fourier transform infrared spectroscopy
Fourier transform infrared spectroscopy (FTIR) was performed on a Perkin Elmer Frontier FTIR spectrometer equipped with a diamond attenuated total reflectance (ATR) attachment. A small amount of the sample was placed in the diamond hole, and its spectrum recorded over the range of 400-4000 cm\(^{-1}\).

3.4.3 \(^1\)H-NMR spectroscopy
\(^1\)H-NMR spectra were recorded on a JEOL FT-NMR lambda 400 MHz spectrometer. The solvent was DMSO-ds. The chemical shifts were reported in ppm using the residual protonated solvent as the reference.

3.4.4 UV-vis spectroscopy
The UV-vis spectra were recorded between 1000-200 nm on a Shimadzu UV-vis-NIR 3600 spectrophotometer. An exactly known mass of a sample was dissolved in a suitable organic solvent in a 10-ml volumetric flask. The solution was placed into a 1-cm quartz cuvette and inserted into the spectrometer holder. The data were collected with the solvent as the background. The molar absorptivity (\(\varepsilon\)) was calculated using the Beer–Lambert’s law: \(A = \varepsilon c \ell\), where \(A\) is the absorbance, \(c\) is the molarity of the solution (mol dm\(^{-3}\)), and \(\ell\) is the path length (1 cm).
3.4.5 **Photoluminescence spectroscopy**

Excitation and emission photoluminescence spectra were recorded on a PTI QuantaMaster™ 40 spectrofluorometer. The sample was held in a quartz fluorescence cuvette ($l = 1 \text{ cm} \times 1 \text{ cm}$) and fluorescence was detected at $90^\circ$ to the excitation beam with the corrected background. The solvent used was DMSO. The emission spectra was measured by exciting the sample at excitation wavelength for each complex and collecting the emitted fluorescence. Slit widths were adjusted for excitation emission.

Fluorescence lifetime measurement was performed on a TimeMaster (TM-200) LED-Based Strobe Lifetime spectrofluorometer obtained from Photon Technology International and using the stroboscopic technique. The observed fluorescence decay was analysed using Felix GX™ data acquisition and analysis software. Data was recorded in 100 ps time intervals within 50 – 70 ns observation window. The instrument response function (IRF) was measured from the scattered light and estimated to be $\sim 1.5$ ns (full width at half maximum). The measured transients were fitted to multiexponential functions convoluted with the system response function. The fitting procedure is based on the Marquardt algorithm where the experimental data are compared to a model decay convoluted with the IRF. The fit was judged by the value of the reduced chi-squared ($\chi^2$).

3.4.6 **Room-temperature magnetic susceptibility**

The mass magnetic susceptibility ($\chi_g$) was recorded at room-temperature (298 K) on a Sherwood automagnetic susceptibility balance by the Gouy method, using distilled water ($0.72 \times 10^{-6}$ c.g.s) as the calibrant. The grinded sample was carefully packed into a narrow cylindrical tube to a length of about 1.5 cm, and its weight was recorded. The corrected molar magnetic susceptibility ($\chi_M^{corr}$) and the effective magnetic moment ($\mu_{\text{eff}}$) were calculated from the following relationships:

$$\chi_M = \chi_g \times (\text{formula weight})$$
where \( T \) is the absolute temperature in Kelvin, \( \chi_{\text{dia}} \) is the diamagnetic correction of the components of the ligands and associated ion, and \( N\alpha \) is the temperature independent paramagnetism of each metal(II) (Appendix). The diamagnetic corrections for cations, anions, and individual atoms and are given in units of \( 10^{-5} \) /g atom.

### 3.4.7 Thermogravimetry

The thermogravimetric analysis (TGA) was recorded from 50 \( ^\circ \text{C} \) to 900 \( ^\circ \text{C} \) on a Perkin-Elmer 4000 TG/DTA thermal instrument with the scan rate of 20 \( ^\circ \text{C} \) min\(^{-1}\). The sample was analysed under \( \text{N}_2 \) gas with a flow rate of 10 cm\(^3\) min\(^{-1}\). An empty alumina pan was placed in the holder and tared. Then the sample (3 - 5 mg) was loaded onto the pan and the weight recorded.

### 3.4.8 Differential scanning calorimetry

The differential scanning calorimetric scan (DSC) was performed on a Mettler Toledo DSC 822. The weight of sample (2-4 mg) in an aluminium pan was initially recorded on a Mettler Toledo microbalance. The sealed aluminum containing the sample was then loaded into the DSC instrument. The sample was heated from 25 \( ^\circ \text{C} \) to about 150 \( ^\circ \text{C} \) at the heating rate of 10 \( ^\circ \text{C} \) min\(^{-1}\), and then cooled from 200\( ^\circ \text{C} \) to 25 \( ^\circ \text{C} \) at the cooling rate of 10 \( ^\circ \text{C} \) min\(^{-1}\) under \( \text{N}_2 \). The onset temperatures were quoted for all peaks observed. The normalized area under each of the heat flow curve was determined using the system software of the instrument.

### 3.4.9 Cyclic voltammetry

The cyclic voltammograms (CV) were recorded on a Gamry Instrument Reference 600 potentiostat/galvanostat/ZRA. Tetra-\( n \)-butylammonium tetrafluoroborate (TBATFB) (0.1 M) was used as the electrolyte, a glassy carbon electrode was used as the working
electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire was used as the counter electrode. The initial and final voltage was 0 V, and the potential range was +1.5 V to -1.5 V. The scan rate was 100 mV s\(^{-1}\). The samples (0.005 M) were prepared in THF and were bubbled with N\(_2\) gas for 1 min prior to the analysis.

3.4.10 Polarizing optical microscopy

The optical textures of selected samples were observed on an Olympus polarizing microscope equipped with a Mettler Toledo FP90 central processor and FN82HT hot stage. A minute amount of the sample was sandwiched between two microscope slides, and then heated at the rate of 5-10 °C min\(^{-1}\), and cooled at the rate of 2-5 °C min\(^{-1}\). The magnification was 50X, and the photomicrographs were captured by the computer connected to the microscope.