

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENT</b>	i
<b>ABSTRACT</b>	ii
<b>ABSTRAK</b>	iv
<b>TABLE OF CONTENTS</b>	vii
<b>LIST OF FIGURE</b>	xi
<b>LIST OF TABLE</b>	xix
<b>LIST OF SCHEME</b>	xx
<b>CHAPTER 1 INTRODUCTION</b>	1
<b>References</b>	3
<b>CHAPTER 2 THEORY AND LITERATURE REVIEW</b>	
<b>2.1 Introduction</b>	4
<b>2.2 Copper(II) Carboxylates</b>	4
<b>2.2.1 Structural elucidation</b>	5
(a) <i>Elemental analyses</i>	7
(b) <i>Fourier transform infrared spectroscopy</i>	8
(c) <i>UV-visible spectroscopy</i>	9
<b>2.2.2 Thermal properties</b>	11
(a) <i>Thermogravimetry</i>	11
(b) <i>Differential scanning calorimetry</i>	13
<b>2.2.3 Magnetism</b>	15
<b>2.2.4 Redox properties</b>	19
<b>2.3 Solar Materials</b>	20

<b>2.3.1 Band gap</b>	22
<b>2.3.2 Photoluminescence spectroscopy</b>	24
<b>References</b>	26
<b>CHAPTER 3 EXPERIMENTAL</b>	
<b>3.1 Materials</b>	29
<b>3.2 Synthesis</b>	31
<b>3.2.1 One-pot reaction</b>	31
(a) $K_2[Cu_2(p-OC_6H_4COO)_2(CH_3CH=CHCOO)_2]$	31
(b) $K[Cu_2(p-OC_6H_4COO)(CH_3CH=CHCOO)_3]$	31
(c) $K_3[Cu_2(p-OC_6H_4COO)_3(CH_3CH=CHCOO)]$	32
(d) $K_2[Cu_2(p-OC_6H_4COO)_2(CH_2=C(CH_3)COO)_2]$	32
(e) $K[Cu_2(p-OC_6H_4COO)(CH_2=C(CH_3)COO)_3]$	32
(f) $K_3[Cu_2(p-OC_6H_4COO)_3(CH_2=C(CH_3)COO)]$	32
<b>3.2.2 Ligand-exchange reaction</b>	33
(a) <i>Synthesis of</i> $[Cu_2(p-HOC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]$	33
(b) $[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3]$	35
(c) $[Cu_2(p-HOC_6H_4COO)((CH_3)_3CCOO)_3]$	36
(d) $[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_3CH(C_2H_5)COO)_3]$	36
(e) $[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_3]$	37
<b>3.2.3 <math>K[Cu_2(p-OC_6H_4COO)(CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3]</math></b>	38
<b>3.3 Instrumental Analyses</b>	
<b>3.3.1 Elemental analyses</b>	39
<b>3.3.2 Fourier transform infrared spectroscopy</b>	39
<b>3.3.3 Ultraviolet-visible spectroscopy</b>	39

3.3.4	<i>Thermogravimetric analysis</i>	40
3.3.5	<i>Differential scanning calorimetry</i>	40
3.3.6	<i>Room-temperature magnetic susceptibility</i>	40
3.3.7	<i>Cyclic voltammetry</i>	41
3.3.8	<i>Photoluminescence spectroscopy</i>	41
3.3.9	<i>Single crystal X-ray crystallography</i>	41
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>		
4.1	<b>Introduction</b>	42
4.2	<b>One-Pot Reaction</b>	46
4.2.1	<b><math>K_n[Cu_2(p-OC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]</math></b>	
(a)	$K_2[Cu_2(p-OC_6H_4COO)_2(CH_3CH=CHCOO)_2]$	46
(b)	$K[Cu_2(p-OC_6H_4COO)(CH_3CH=CHCOO)_3]$	60
(c)	$K_3[Cu_2(p-OC_6H_4COO)_3(CH_3CH=CHCOO)]$	71
(d)	<i>Summary</i>	71
4.2.2	<b><math>K_n[Cu_2(p-OC_6H_4COO)_n(CH_2=C(CH_3)COO)_{4-n}]</math></b>	
(a)	$K_2[Cu_2(p-OC_6H_4COO)_2(CH_2=C(CH_3)COO)_2]$	73
(b)	$K[Cu_2(p-OC_6H_4COO)(CH_2=C(CH_3)COO)_3]$	78
(c)	$K_3[Cu_2(p-OC_6H_4COO)_3(CH_2=C(CH_3)COO)]$	83
(d)	<i>Summary</i>	88
4.3	<b>Ligand-Exchange Reaction</b>	90
4.3.1	<b><math>[Cu_2(p-HOC_6H_4COO)_n(CH_3CH=CHCO)_{4-n}]</math></b>	
(a)	$[Cu_2(p-HOC_6H_4COO)_2(CH_3CH=CHCO)_2]$	93
(b)	$[Cu_2(p-HOC_6H_4COO)(CH_3CH=CHCO)_3]$	102
(c)	$[Cu_2(p-HOC_6H_4COO)_3(CH_3CH=CHCO)]$	109
(d)	<i>Summary</i>	111

4.3.2	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_7CH=CH(CH_2)_7COO)_3]$	112
4.3.3	$[Cu_2(p-HOC_6H_4COO)((CH_3)_3CCOO)_3]$	119
4.3.4	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_3CH(C_2H_5)COO)_3]$	128
4.3.5	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_3]$	134
4.3.6	<i>Summary</i>	140
4.4	Conversion to Ionic Complex	142
4.5	Photoluminescence Spectroscopy	146
	References	149

## CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1	Conclusions	151
5.2	Suggestions for Future Works	152

### Appendices

## LIST OF FIGURE

<b>Figure</b>	<b>Description</b>	<b>Page</b>
Figure 2.1	The paddle-wheel structure of $[\text{Cu}_2(\text{RCOO})_4]$	5
Figure 2.2	Coordination modes of $\text{RCOO}^-$ anion	5
Figure 2.3	Structure of (a) $\text{bis}(\mu\text{-diphenylacetato-}O:O')$ dicopper(II); and (b) <i>catena</i> -poly[[ $\text{bis}(\mu\text{-diphenylacetato-}O:O')$ dicopper] $(\mu_3\text{-diphenylacetato-}1\text{-}O:2\text{-}O':1'\text{-}O')$ $(\mu_3\text{-diphenylacetato-}1\text{-}O:2\text{-}O':2'\text{-}O')$ ]] (showing only the linkage at the centres)	6
Figure 2.4	Structure of (a) $\text{tetrakis}(\mu\text{-}1\text{-phenylcyclopropane-}1\text{-carboxylato-}O,O')$ $\text{bis}(\text{ethanol-}O)$ dicopper(II); and (b) $\text{poly}[\text{tetrakis}(\mu\text{-}1\text{-phenylcyclopropane-}1\text{-carboxylato-}O,O')$ $\text{bis}(\text{ethanol-}O)$ dicopper(II)] (showing only the linkage at the centres)	7
Figure 2.5	Colour wheel	9
Figure 2.6	geometry at the copper center (a) tetrahedral; (b) square pyramidal; and (c) square planar	10
Figure 2.7	The energy of the <i>d</i> orbitals in a square planar copper(II) centre	11
Figure 2.8	TGA of calcium oxalate ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ )	12
Figure 2.9	Structure of $[\text{Cu}_2(\text{C}_6\text{H}_4\text{COO})_4(\text{EtOH})_2]$	13
Figure 2.10	Features and assignation of DSC curve	14
Figure 2.11	Structure of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_4]$	14

Figure 2.12	Structure of tetrakis( $\mu$ -(2,2-(dioctyl(acetate))- <i>O,O'</i> )bis(copper(II)))-	15
Figure 2.13	Alignment of electrons in a sample: (a) paramagnetic; (b) diamagnetic	16
Figure 2.14	Electron alignment in a paramagnetic sample: (a) antiferromagnetism; (b) ferromagnetism; (c) ferrimagnetism	16
Figure 2.15	Structure of $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$	18
Figure 2.16	Cyclic voltammogram of a reversible process	20
Figure 2.17	Energy arrangement in atoms	22
Figure 2.18	Jablonski diagram	24
Figure 3.1	Structural formulas of the carboxylic acids used for the synthesis of ionic copper(II) mixed carboxylates	30
Figure 3.1	Structural formula of (a) $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_4]$ ; and (b) $[\text{Cu}_2\text{CH}_3(\text{CH}_2)_7)_2\text{CHCOO})_4]$	43
Figure 3.1	Structural formula of a copper(I) complex with 1,8- naphthalenedithiolate	44
Figure 3.1	Structural formula of a copper(I) complex with 2,9- phenylethynyl-1,10-phenantroline	44
Figure 3.1	FTIR spectrum of <b>Complex 1</b>	47
Figure 3.1	FTIR spectrum of <i>p</i> -HOC <sub>6</sub> H <sub>4</sub> COOH	47
Figure 3.1	FTIR spectrum of CH <sub>3</sub> CH=CHCOOH	48
Figure 3.1	UV of <b>Complex 1</b> in (a) solid; and (b) solution	48

Figure 4.8	Assignment of electronic transitions for a square pyramidal <b>Complex 1</b> (not to scale)	49
Figure 4.9	Proposed structural formula of <b>Complex 1</b> ( $K^+$ ion and $H_2O$ solvate are not shown)	49
Figure 4.10	TGA of <b>Complex 1</b>	50
Figure 4.11	DSC of <b>Complex 1</b>	51
Figure 4.12	CV of <b>Complex 1</b>	52
Figure 4.13	Structural formula of $[Cu(CH_3COO)_2(2,2'-bipy)] [10]$	53
Figure 4.14	FTIR of <b>Complex 2</b>	54
Figure 4.15	UV of <b>Complex 2</b> in (a) solid; and (b) solution	55
Figure 4.16	Proposed structural formula of <b>Complex 2</b> , showing the <i>trans</i> - isomer)	56
Figure 4.17	TGA of <b>Complex 2</b>	57
Figure 4.18	DSC of <b>Complex 2</b>	58
Figure 4.19	CV of <b>Complex 2</b>	59
Figure 4.20	FTIR of <b>Complex 3</b>	61
Figure 4.21	UV-vis spectrum of <b>Complex 3</b> (a) as a solid; and (b) in solution	61
Figure 4.22	Proposed structural formula of <b>Complex 3</b>	62
Figure 4.23	TGA of <b>Complex 3</b>	63
Figure 4.24	DSC of <b>Complex 3</b>	64
Figure 4.25	CV of <b>Complex 3</b>	65
Figure 4.26	FTIR of <b>Complex 4</b>	66
Figure 4.27	The UV-vis spectrum of <b>Complex 4</b> (a) as a solid; and (b) in solution	67

Figure 4.28	Proposed structural formula of <b>Complex 4</b>	67
Figure 4.29	TGA of <b>Complex 4</b>	68
Figure 4.30	DSC of <b>Complex 4</b>	69
Figure 4.31	CV of <b>Complex 4</b>	70
Figure 4.32	FTIR of dark brown powder	71
Figure 4.33	FTIR of <b>Complex 5</b>	74
Figure 4.34	FTIR of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	74
Figure 4.35	UV-vis spectrum of <b>Complex 5</b> (a) as a solid; and (b) in solution	75
Figure 4.36	Proposed structural formula of [ <b>Complex 5</b> ] <sup>-</sup> ( $\text{K}^+$ ions are not shown)	75
Figure 4.37	TGA of <b>Complex 5</b>	76
Figure 4.38	DSC of <b>Complex 5</b>	77
Figure 4.39	CV of <b>Complex 5</b>	78
Figure 4.40	FTIR of <b>Complex 6</b>	79
Figure 4.41	UV-vis of <b>Complex 6</b> (a) as a solid; and (b) in solution	80
Figure 4.42	Proposed structural formula of <b>Complex 6</b>	80
Figure 4.43	TGA of <b>Complex 6</b>	81
Figure 4.44	DSC of <b>Complex 6</b>	82
Figure 4.45	CV of <b>Complex 6</b>	83
Figure 4.46	FTIR of <b>Complex 7</b>	84
Figure 4.47	UV-vis spectrum of <b>Complex 7</b> (a) as a solid; and (b) in solution	84
Figure 4.48	Proposed structural formula of <b>Complex 7</b>	85
Figure 4.49	TGA of <b>Complex 7</b>	86

Figure 4.50	DSC of <b>Complex 7</b>	87
Figure 4.51	CV of <b>Complex 7</b>	88
Figure 4.52	FTIR of $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})_4]$	90
Figure 4.53	An ORTEP presentation of the blue crystal	91
Figure 4.54	The packing pattern of blue crystal, viewed along the crystallographic <i>c</i> -axis	91
Figure 4.55	FTIR of <b>Complex 8</b>	94
Figure 4.56	FTIR of $[\text{Cu}_2(\text{CH}_3\text{CH}=\text{CHCOO})_4]$	95
Figure 4.57	UV-vis of <b>Complex 8</b> in (a) solid; and (b) solution	96
Figure 4.58	Proposed structural formula of <b>Complex 8</b>	96
Figure 4.59	TGA of <b>Complex 8</b>	97
Figure 4.60	DSC of <b>Complex 8</b>	98
Figure 4.61	CV of <b>Complex 8</b>	99
Figure 4.62	FTIR of <b>Complex 9</b>	101
Figure 4.63	UV-vis spectrum of <b>Complex 9</b> (a) as a solid; and (b) in solution	101
Figure 4.64	Proposed structural formula of <b>Complex 9</b> (non-coordinated $\text{H}_2\text{O}$ molecules are not shown)	102
Figure 4.65	FTIR of <b>Complex 10</b>	103
Figure 4.66	UV-vis spectrum of <b>Complex 10</b> (a) as a solid; and b) in solution	104
Figure 4.67	Proposed structural formula of <b>Complex 10</b>	104
Figure 4.68	TGA of <b>Complex 10</b>	105

Figure 4.69 DSC of <b>Complex 10</b>	106
Figure 4.70 CV of <b>Complex 10</b>	108
Figure 4.71 FTIR spectrum of green powder	109
Figure 4.72 FTIR spectrum of the purple powder	110
Figure 4.73 FTIR spectrum of green powder	111
Figure 4.74 FTIR spectrum of <b>Complex 11</b>	113
Figure 4.75 FTIR spectrum of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_4]$ (starting material)	114
Figure 4.76 UV-vis spectrum of <b>Complex 11</b> in methanol	114
Figure 4.77 Proposed structural formula of <b>Complex 11</b>	115
Figure 4.78 TGA of <b>Complex 11</b>	116
Figure 4.79 DSC of <b>Complex 11</b>	117
Figure 4.80 CV of <b>Complex 11</b>	118
Figure 4.81 FTIR of <b>Complex 12</b>	120
Figure 4.82 FTIR of $[\text{Cu}_2((\text{CH}_3)_3\text{CCOO})_4]$ (starting material)	120
Figure 4.83 UV-vis spectrum of <b>Complex 12</b> in solution	121
Figure 4.84 Proposed structural formula of <b>Complex 12</b> (pyridinium ion is not shown)	122
Figure 4.85 TGA of <b>Complex 12</b>	122
Figure 4.86 DSC of <b>Complex 12</b>	123
Figure 4.87 CV of <b>Complex 12</b>	124
Figure 4.88 An ORTEP presentation of <b>Complex 13</b>	126
Figure 4.89 The packing pattern of <b>Complex 13</b> , viewed along the crystallographic <i>b</i> -direction.	126
Figure 4.90 FTIR of <b>Complex 14</b>	129

Figure 4.91	FTIR of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_4]$ (starting material)	129
Figure 4.92	UV-vis spectrum of <b>Complex 14</b> (a) as a solid; (b) in solution	130
Figure 4.93	Proposed structural formula of <b>Complex 14</b> ( $\text{CH}_3\text{CH}_2\text{OH}$ solvates are not shown; two dimers are shown to show square pyramidal Cu(II) centres)	130
Figure 4.94	TGA of <b>Complex 14</b>	131
Figure 4.95	DSC of <b>Complex 14</b>	132
Figure 4.96	CV of <b>Complex 14</b>	133
Figure 4.97	FTIR spectrum of <b>Complex 15</b>	135
Figure 4.98	FTIR spectrum of $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_5\text{CH}_3)\text{COO})_4]$ (starting material)	135
Figure 4.99	UV-vis spectrum of <b>Complex 15</b> (a) as a solid; (b) in solution	136
Figure 4.100	Proposed structural formula of <b>Complex 15</b>	137
Figure 4.101	TGA of <b>Complex 15</b>	138
Figure 4.102	DSC of <b>Complex 15</b>	139
Figure 4.103	CV of <b>Complex 15</b>	140
Figure 4.104	FTIR spectrum of <b>Complex 17</b>	143
Figure 4.105	UV-vis spectrum of <b>Complex 17</b> in methanol	143
Figure 4.106	Proposed structural formula of <b>Complex 17</b>	144
Figure 4.107	TGA of <b>Complex 17</b>	145

Figure 4.108 DSC of <b>Complex 17</b>	145
Figure 4.109 PL spectrum of (a) <b>Complex 1</b> ; (b) <b>Complex 2</b> ; (c) <b>Complex 3</b> ; (d) <b>Complex 4</b> ; (e) <b>Complex 6</b> ; (f) <b>Complex 7</b> ; (g) <b>Complex 8</b> ; and (h) <b>Complex 15</b>	147
Figure 5.1 Structural formulas of organic cations	153
Figure 5.2 Conjugated ligands	153

## LIST OF TABLE

<b>Table</b>	<b>Description</b>	<b>Page</b>
Table 4.1	FTIR data and assignment for <b>Complex 2</b>	54
Table 4.2	Analytical results for complexes from the one-pot reaction	72
Table 4.3	Analytical results for complexes from the one-pot reaction	89
Table 4.4	Crystallographic and refinement details of blue crystal	92
Table 4.5	Hydrogen bonds [ $\text{\AA}$ and deg.] of blue crystal	92
Table 4.6	Analytical results for complexes from the ligand-exchange reaction	112
Table 4.7	Crystallographic and refinement details of <b>Complex 13</b>	127
Table 4.8	Selected bond lengths [ $\text{\AA}$ ] of <b>Complex 13</b>	128
Table 4.9	Hydrogen bonds [ $\text{\AA}$ and deg.] of <b>Complex 13</b>	128
Table 4.10	Complexes from the ligand-exchange reaction	141
Table 4.11	The PL data	148

## LIST OF SCHEME

<b>Scheme</b>	<b>Description</b>	<b>Page</b>
Scheme 2.1	Thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	12
Scheme 4.1	EC mechanism of <b>Complex 8</b>	99
Scheme 4.2	Redox process of <b>Complex 10</b>	108
Scheme 4.3	The ECE mechanism of <b>Complex 12</b>	125
Scheme 4.4	Redox process of <b>Complex 14</b>	133