TABLE OF CONTENTS

	Page
Acknowledgement	iii
Abstract (in English)	v
Abstract (in Thai)	vii
List of Tables	xiii
List of Figures	xv
Abbreviations and symbols	xxi
CHAPTER 1 INTRODUCTION	1
1.1 General introduction to supramolecular interactions	5
1.1.1 Hydrogen bond	5
1.1.2 Halogen bond	7
1 1.3 Aromatic π - π interactions	9
1.1.4 Aliphatic CH/ π interactions	11
1.2 Synthesis and single crystal growth techniques	14
1.2.1 Diffusion method	14
1.2.2 Solvo(hydro)thermal synthesis	-15
1.2.3 Microwave-assisted synthesis	16
1.2.4 Ionothermal synthesis	ni 18-rsi
1.3 Polycarboxylate and amino acids as ligands	19
1.4 Research objectives	23 E

1.5 Research plan	24
CHAPTER 2 NEW POLYMORPH OF 1,3,5-TRIAZINE-2,4,6-	30
TRIAMINEHEXAACETIC ACID	
2.1 Experimental	31
2.1.1 Microwave–assisted crystal growth of TTHA–II	31
2.1.2 Structure determination and refinement	32
2.1.3 Vibrational and electronic spectroscopic study of TTHA-II	33
2.2 Results and discussion	34
2.2.1 Crystal structure and hydrogen bonding network analysis of	34
TTHA-II	
2.2.2 Spectroscopic study of TTHA–II	40
2.3 Conclusions	41
CHAPTER 3 NEW TRINUCLEAR Ni ^{II} COMPLEX CONTAINING	44
INCOMPLETE CUBANE Ni ₃ O ₄ CORE STRUCTURE	
3.1 Experimental	45
3.1.1 Synthesis and crystal growth	45
3.1.2 Single crystal structure determination	45
3.2 Results and discussion	51
3.3 Conclusions	57
CHAPTER 4 A CHIRAL DECORATED METAL-NICOTINATE	61
FRAMEWORK	
4.1 Experimental	62

4.1.1 Microwave-assisted hydrothermal crystal growth and initial	62
characterization	
4.1.2 Structure determination and refinement	63
4.2 Results and discussion	68
4.2.1 Description of crystal structures	68
4.2.2 The FT–IR spectrum and thermal behaviors	73
4.3 Conclusions	75
CHAPTER 5 IONOTHERMAL SYNTHESIS AND CRYSTAL	77
STRUCTURES OF NEW d ¹⁰ BLUE LUMINESCENT	
METAL-ORGANIC MATERIALS	
5.1 Experimental	79
5.1.1 Synthesis and characterization	79
5.1.2 Single crystal structure determination	80
5.1.3 Structure and property of the de-intercalated samples	86
5.2 Results and discussion	86
5.2.1 Crystal structures description	86
5.2.2 Thermogravimetric analysis	97
5.2.3 UV–Vis and photoluminescent spectroscopic studies	98
5.2.4 Stability and photoluminescence property of the	101
de-intercalated IV- <i>L</i> and V - <i>L</i>	
5.3 Conclusions	106
CHAPTER 6 CONCLUSIONS	

APPENDICES

APPENDIX A: NOTATIONS FOR LIGATING ATOMS IN 113 COORDINATION COMPLEXES

APPENDIX B: BAND GAP ENERGY DETERMINATION *VIA* TAUC 116 METHOD

CURRICULUM VITAE

118

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved

LIST OF TABLES

LIST OF TABLES			
	Table		Page
	1.1	Classification of hydrogen bonding interactions.	5
	1.2	Distance and orientation dependence of the CH/ π interactions.	12
	2.1	Crystal and experimental data for TTHA-I and TTHA-II.	33
	2.2	Selected geometric parameters for TTHA-II.	34
	2.3	Details of the hydrogen bonding interactions in TTHA-II. A	37
		hydrogen bond donor and acceptor are denoted as D and A,	
		respectively.	
	3.1	Crystallographic data for structural solution and refinement of I .	46
	3.2	Atomic coordinates and equivalent isotropic displacement parameters	47
		of non-hydrogen atoms for I .	
	3.3	Selected observed bond distances and angles in the compound I.	50
	3.4	Hydrogen bonding geometry for I .	55
	4.1	Crystal and experimental data for II and III.	64
	4.2	Atomic coordinates and equivalent isotropic displacement parameter	65
		for II.	
	4.3	Atomic coordinates and equivalent isotropic displacement parameter	66
		for III.	
	4.4	Selected bond distances and angles in II .	67

4.5	Selected bond distances and angles in III.	67
4.6	Details of the hydrogen bonding interactions in II. A hydrogen bond	71
	donor and acceptor atoms are denoted as D and A, respectively.	
5.1	Crystal and experimental data for IV and V.	81
5.2	Atomic coordinates and equivalent isotropic displacement parameter	82
	for IV.	
5.3	Atomic coordinates and equivalent isotropic displacement parameters	83
	for V.	
5.4	Selected geometric parameters for IV.	85
5.5	Selected geometric parameters for V.	85
5.6	Details of the hydrogen bonding interactions in IV. A hydrogen bond	94
	donor and acceptor are defined as D and A, respectively.	
5.7	FT–IR and Raman assignments for IV, V, IV– <i>L</i> and V– <i>L</i> .	96

ลิ<mark>ปสิทธิ์มหาวิทยาลัยเชียงใหม่</mark> Copyright[©] by Chiang Mai University All rights reserved

LIST OF FIGURES

Page

2

3

6

Figure

- 1.1 Metal-organic materials encompass discrete (0-D) as well as extended structures with periodicity in one (1-D), two (2-D) and three (3-D) dimensions.
- 1.2 Representation of (a) 1–D, (b) 2–D and (c) 3–D MOMs.
- 1.3 Appropriate choices of ligands in providing (a) coordination compounds and (b) coordination networks.
- 1.4 Representation of hydrogen bonding interactions (dotted line) of (a) $[Co^{II}(C_2H_2N_2)_3]SO_4$ [19] and (b) M₃(BTC)₂·12H₂O.
- 1.5 Diagrams showing the presence of halogen bond (dotted line) in a 8 series of Hg(II) complexes.
- 1.6 Representations of (a) the presence of halogen bonds in the zigzag
 9 chain structure of the co-crystals of (1,2-diiodoterfluorobenzene).
 (phenazine) and (b) the halogen and hydrogen bonds in the structure of (2-mercapto-1-methylimidazole)·(1,2-diiodoterfluorobenzene).
- 1.7 Principal orientations of aromatic–aromatic or $\pi \pi$ interactions.

- 1.8 Representation of (a) $\pi \pi$ and CH··· π interactions in 10 [Ni(Phen)₂(H₂O)₂][Ni(PtcH)₂]·11H₂O and (b) the 2–D framework structure with hydrophilic cavities formed by strong $\pi \pi$ and CH··· π interactions.
- 1.9 Formation of two isomeric supramolecular architectures. Each isomer 11 consists of 2–D honeycomb layers based on 4,4',4''–(2,4,6– trimethylbenzene–1,3,5–triyl)tribenzoic acid (H₃TMTA) and Zn₂(COO)₃ SBUs.
- 1.10 Representation of the existence of the aliphatic CH/π interactions in 13 the crystal structure of $\{[Zn(L)_2Cl_2]\cdot DMF\cdot CH_3OH\}_n$; L is 1,4-bis(benzimidazol-1-ylmethyl)benzene.
- 1.11 Representation of (a) crystal packing of the acetate compound
 13 showing the 3–D network of microchannels (backbone blur) and (b) a cavity with the aliphatic chains pointing toward it.
- 1.12 Representation of (a) liquid diffusion and (b) vapor diffusion methods. 14
- 1.13 Diagram showing the components of general hydrothermal reactor. 16
- 1.14 Dipolar molecules trying to align with an oscillating electric field of 17 microwave component.
- 1.15 Some typical cations and anions commonly used as the component of 18 ILs.
- 1.16 Diagrams showing different coordination modes of carboxylate groups.
- 1.17A large series of isoreticular IRMOFs.20

- 1.18 Coordination modes of TTHA in (a) $\{Na_2[Co_3(H_2TTHA)_2(H_2O)_{12}]-$ 22 (H₂O)₂ $\}\cdot 4H_2O$, (b) $\{Na[Cu_4(H_2TTHA)(HTTHA)(H_2O)_8](H_2O)_3\}\cdot$ 5H₂O, (c) $[Cd_3(TTHA)(H_2O)_4]$ and (d) $[Ca_5(HTTHA)_2(H_2O)_8].$
- 2.1 ORTEP drawing of molecular unit in **TTHA–II** showing atom 35 numbering scheme and 70% probably displacement ellipsoids for non–hydrogen atoms. Symmetry code: (i) x, y, 1.5 z.
- 2.2 Hydrogen bonding interactions (dotted lines) in **TTHA–II** illustrated 36 by (a) capped stick model showing intermolecular interactions, (b) 70% thermal ellipsoids showing intramolecular interactions, and (c) capped stick model showing the packing of molecular units. Symmetry codes: (i) - x, y, 1.5 - z; (ii) - x, 2 - y, 2 - z; (iii) x, 2 - y, 0.5 +z; (iv) 0.5 - x, -0.5 + y, 2.5 - z; (v) 0.5 - x, 2.5 - y, 2 - z; (vi) - 0.5 + x, 2.5 - y, - 0.5 + z; (vii) - 0.5 - x, 2.5 - y, 1 - z.
- 2.3 Crystal packing in **TTHA–II** showing (a) face–to–face π –stacking 39 and (b) molecular columns built up from the stacking of the molecules in *c*–direction.
- 2.4 Simulated X-ray diffraction patterns of (a) **TTHA-I** and (b) 39 **TTHA-II**.
- 2.5 FT–IR spectrum collected on the ground crystals of TTHA–II.
- 2.6
 UV-Vis spectrum collected on a suspension of the ground TTHA-II
 41

 crystals in methyl alcohol.
 41

- 3.1 The asymmetric unit of I showing atom–labeling scheme and with 52
 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.
- 3.2 The incomplete cubane core of **I**. Only selected atoms from the 53 ligands are drawn. Atoms are shown as 30% probability ellipsoids.
- 3.3 View of (a) intra-cluster and (b) inter-cluster hydrogen bonding 56 interactions (dash lines), showing the donor and acceptor atoms by ball-and-stick model and with 50% probability displacement ellipsoids for the incomplete cubane core. Weak C–H…O hydrogen bonding interactions are omitted.
- 4.1 View of extended asymmetric units of (a) II and (b) III with 50% 68 thermal ellipsoids and atomic labeling for non-hydrogen atoms. The hydrogen bond shows in dotted lines. Symmetry code: (i) x 1, y, z 1.
- 4.2 Illustration of the one-dimensional coordination polymer 69 $[Co(C_9H_{10}NO_3)(C_6H_4NO_2)(H_2O)_2]_n$ chain within **II**. Color scheme: Ni, black; O, dark grey; N, light grey; C, grey.
- 4.3 Views of (a) ABAB stacking of the $[Co(C_9H_{10}NO_3)(C_6H_4NO_2)$ 70 $(H_2O)_2]_n$ chains parallel to the *b*-axis and (b) checkerboard arrangement of the chains along [1 0 1] direction.
- 4.4 Representation of the hydrogen bonding interactions (dotted lines) in 72 II, generated by (a) - x, $y - \frac{1}{2}$, -z, (b) - x, $y - \frac{1}{2}$, -z + 1 and (c) x - 1, y, z and x, y, z + 1.

4.5 FT–IR spectra collected on the ground crystals of (a) **II** and (b) **III**.

- 4.6 Thermogravimetric analysis of (a) **II** and (b) **III**.
- 5.1 Views of the extended asymmetric units of (a) **IV** and (b) **V**, showing 87 the tetrahedral–octahedral–tetrahedral trimers. Thermal ellipsoids are shown with 60% probability, and hydrogen atoms are omitted for clarity. Symmetry codes: (i) 2 x, -1 y, -z; (ii) 2 x, -y, -z; (iii) $\frac{1}{2} + x$, $\frac{1}{2} y$, $\frac{1}{2} + z$; (iv) x, 1 + y, 1 + z; (v) x, -1 + y, -1 + z; (vi) 1 x, -y, 1 z; (vii) 2 x, 1 y, 2 z.
- 5.2 Views of the extended layered structure of (a) **IV** and (b) **V**, showing 89 spatial arrangements of the extraframework cations and C-H···O hydrogen bonding interactions (dotted lines). Symmetry codes: (i) $\frac{1}{2}$ + x, $\frac{1}{2}$ y, $\frac{1}{2}$ + z; (ii) $\frac{3}{2}$ x, $\frac{1}{2}$ + y, $\frac{1}{2}$ z.
- 5.3 The (3,6) uninodal net of **hxl** topology or triangular grid of the 91 isoreticular (a) **IV** and (b) **V**.
- 5.4 The ABAB stacking of the two-dimensional in IV, intercalated by the 92 extraframework EMIm⁺ cations.
- 5.5 The ABAB stacking of the two-dimensional in V, intercalated by the 93 extraframework BMIm⁺ cations.

5.6FT–IR spectra of (a) IV and (b) V.955.7Raman spectra of (a) IV and (b) V.955.8Thermogravimetric curve collected on the ground crystals of (a) IV97

and (b) V.
5.9 UV–Vis spectra of (a) EMIm–Cl, (b) H₂BDC and (c) IV.

UV–Vis spectra of (a) BMIm–Cl, (b) H₂BDC and (c) V.

5.10

99

74

- 5.11 Plots of $(\alpha hv)^2$ value versus photon energy (hv) for (a) **IV** and (b) **V**. 100
- 5.12 Photoluminescent spectra of (a) H_2BDC , (b) **IV** and (c) **V**. 101
- 5.13 PXRD patterns calculated from single crystal data of (a) **IV** compared 102 with those collected on the bulk samples of (b) **IV** and (c) the de–intercalated **IV–L**.
- 5.14 PXRD patterns calculated from single crystal data of (a) V compared 102 with those collected on the bulk samples of (b) V and (c) the de-intercalated V-L.
- 5.15 FT–IR spectra of the de–intercalated (a) **IV–L** and (b) **V–L**. 103
- 5.16 Raman spectra of the de-intercalated (a) **IV-L** and (b) **V-L**. 104
- 5.17 Thermogravimetric curves of the de-intercalated (a) IV-L and (b) 105
 V-L, compared with those of the prior de-intercalated c) IV and (d)
 V, respectively.
- 5.18 Photoluminescent spectra of (a) H₂BDC, the de-intercalated (b) IV-L 105 and (c) V-L, compared with those of the prior de-intercalated (d) IV and (e) V, respectively.
- A.1 Diagrams showing typical coordination modes of (a) carboxylate 113 groups and (b) 1,4–benzenedicarboxylate with corresponding notations.
- A.2 Diagrams showing typical coordination modes of L-p-tyrosinate 114 ligands with corresponding notations.

ABBREVIATIONS AND SYMBOLS

atm	atmosphere
BMIm	1-butyl-3-methylimidazolium
ca.	circa (approximately)
calc.	calculation
cm	centimeter
cm ³	cubic centimeter
e.g.	exempli gratia (for exampled)
et al.	et alibi
etc.	et cetara
eV	electron volt
EMIm	1-ethyl-3-methylimidazolium
FT–IR	fourier transform infrared spectroscopy
g	gram
H ₂ BDC	1,4-benzenedicarboxylic acid (terephthalic acid)
i.e.	<i>id est</i> (that is)
ILs	ionic liquid solvents
IUPAC	International Union of Pure and Applied Chemistry
K	Kelvin Kelvin
kHz Q	kilohertz reserveo
K/s	Kelvin per second

mA	milliampere
MHz	megahertz
min	minute
mm	millimeter
MOMs	metal-organic materials
nm	nanometer
n/a	not available
PXRD	powder X-ray diffractometry
	temperature
TTHA	1,3,5-triazine-2,4,6-triaminehexaacetic acid
Tyr	tyrosine
vs.	versus
UV–Vis	ultraviolet-visible spectroscopy
W	Watt
Å	angstrom
°C	degree Celsius
%	percent
θ	theta
p	density
μm	micrometer
1-D	one-dimensional
2–D	two-dimensional
3-D 8 h	three-dimensional eserve

xxii