CHAPTER 1

INTRODUCTION

Research areas relating to metal–organic materials (MOMs) have grasped wide interest from both academic and technological extremes. This is partially due to the novelty and diversity of potential applications they can offer. The beauty and complexity in structures and topologies of MOMs add also motivation for an extensive investigation [1–6]. MOMs, which are also known by other names such as inorganic–organic hybrid materials (IOHs), metal–organic coordination polymers (MOCPs), coordination polymers (CPs) and metal–organic frameworks (MOFs), can be classified into two major groups depending on structural dimensionality of the solid state structure, as illustrated in Fig. 1.1 [7, 8]. Between the two groups, those exhibiting extended framework structures have gained better interest. In order to be successful in yielding MOMs of new framework structures, the understanding of interactions between structural components is critical. The major interaction in the fabrication of new MOMs is undeniably coordinate covalent bond, which is formed by a donation of lone pair electrons of ligands (as Lewis base) to metal ions (as Lewis acid) [9]. The other weak supramolecular interactions such as hydrogen bonding, halogen bonding, π–π stacking, aliphatic CH/π and metal–metal interactions nonetheless play a significant role in directing the architecture and supramolecular assembly in the solid state. These weak interactions can impart influences on the dimension of MOMs as well as their properties such as fluorescent, magnetic and thermal behaviours [10, 11]. The understanding and utilization of weak interactions are therefore of fundamental importance for a development of crystal structures of MOMs.

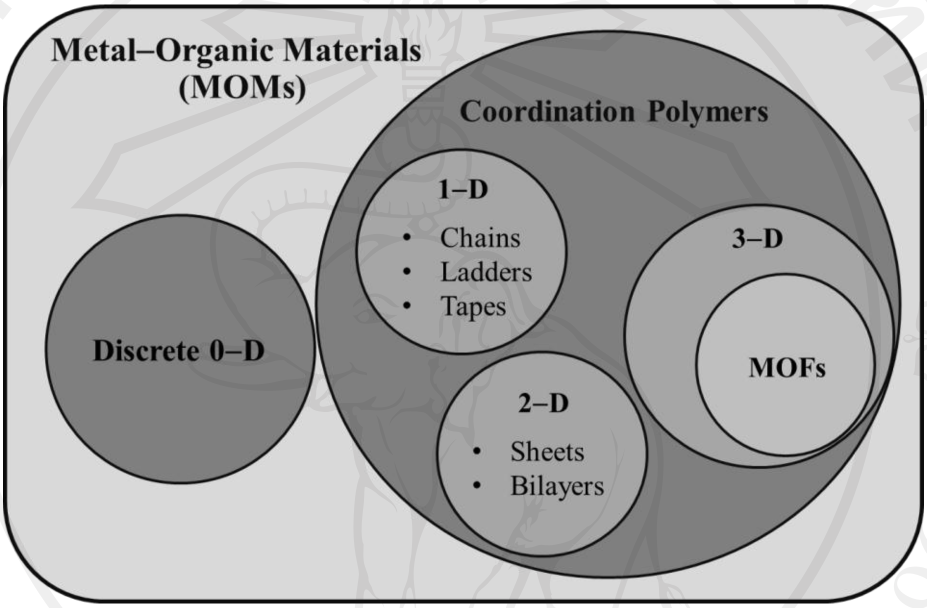

Fig. 1.1 Metal–organic materials encompass discrete (0–D) as well as extended structures with periodicity in one (1–D), two (2–D) and three (3–D) dimensions [8].

Fig. 1.2 shows typical 1–D, 2–D and 3–D polymeric structures of MOMs. There are various factors determining dimensionally of the derived structures, including the nature of metal ions and organic ligands as well as the supramolecular interactions [11–14]. Regarding MOMs with polymeric structures, the basic idea is the expanding coordination in at least one dimension. "Node and spacer" approach where metal ions serve as nodes and organic ligands as spacers or linkers, are generally used in designing and describing the networks [8, 13, 14]. The use of metal ion coordinating to polydentate diverging ligands instead of the converging chelating ligands, for example, provides the extended networks, as schematically depicted in Fig. 1.3.

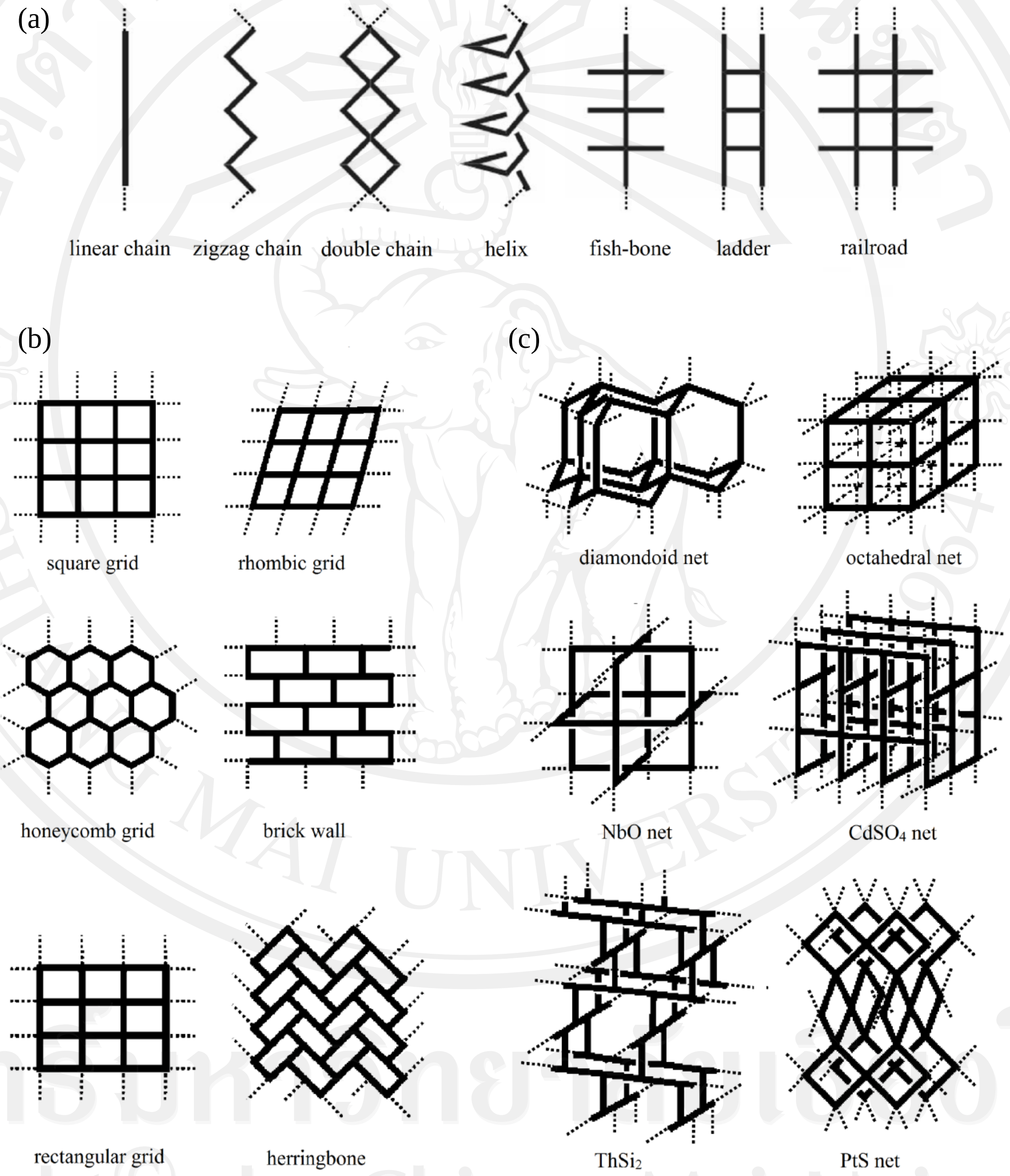

Fig. 1.2 Representation of (a) 1−D, (b) 2−D and (c) 3−D MOMs [12].

According to a vast variety of metal coordination geometries as well as a large number of organic ligands with different functionalities, a design and synthesis of MOMs with desirable structures and properties can be achieved. A selection of appropriate organic ligands is a key factor for determining a success of the construction. This involves not only the functionality but also the geometry of the organic molecules; including conformation of the ligand backbone, orientation of the functional group and steric effect [15]. Crystal design and engineering of MOMs is at the intersection of the “top down” and “bottom up” technologies. Crystal engineering is the planned synthesis of an organic or metal−organic structure associated with a pre−desired property. Since, MOMs contain both metal and organic moieties as integral parts of the structure, if one can predict and control, then one can in principle control the properties of the derived solids too. The concept of crystal design moves therefore from structure design to property design. However, the practical solid product usually differs from case to case [13].

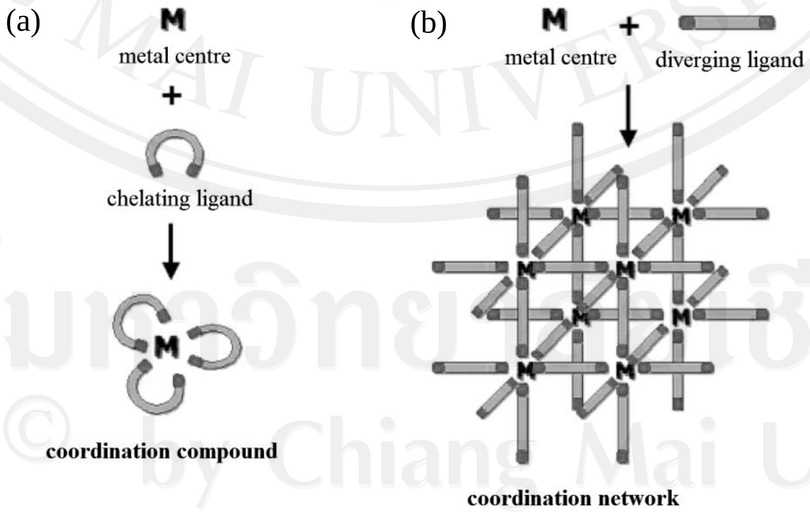

Fig. 1.3 Appropriate choices of ligands in providing (a) coordination compounds and (b) coordination networks [14].

1.1 General introduction to supramolecular interactions

1.1.1 Hydrogen bond

Hydrogen bond is one of the most important non–covalent interactions that involve in both inter– and intra–molecular interactions. Despise controversial definitions of hydrogen bonding interactions, it can be roughly defined as “an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms Y–Z in the same or a different molecule, in which there is evidence of bond formation”. The typical hydrogen bond can be represented using three dots; X–H···Y–Z, where X–H and Y–Z are hydrogen bonding donor and acceptor, respectively [16, 17]. Hydrogen bonding interactions have been classified into three categories, including the very strong, strong and weak interations, based on the distance between the elements X and Y and the X–H···Y angular (Table 1.1).

Table 1.1 Classification of hydrogen bonding interactions [17].

Hydrogen bonds, X–H···Y–Z				
Strength	Examples	X–Y (Å)	H···Y (Å)	X–H···Y (°)
Very strong				
D–H ~ H···A	[F–H–F]$^-$	2.2–2.5	1.2–1.5	175–180
Strong				
D–H < H···A	O–H···O–H	2.6–3.0	1.6–2.2	145–180
	O–H···N–H	2.6–3.0	1.7–2.3	140–180
	N–H···O=C	2.8–3.0	1.8–2.3	150–180
	N–H···O–H	2.7–3.1	1.9–2.3	150–180
	N–H···N–H	2.8–3.1	2.0–2.5	135–180
Weak				
D–H << H···A	C–H···O	3.0–4.0	2.0–3.0	110–180

In the context of MOMs, both the classical O–H···O and N–H···O types as well as the very weak C–H···O interactions dominate in crystal packing (Fig. 1.4); $[M(H_2biIm)_3][M(BTC)(HbiIm)]\cdot 2H_2O$ (M = Co, Ni) [18], $M_3(BTC)_2\cdot 12H_2O$ (M = Co, Ni, and Zn) [19] and $[Co^{II}(C_2H_2N_2)_3]SO_4$ [20], for instances.

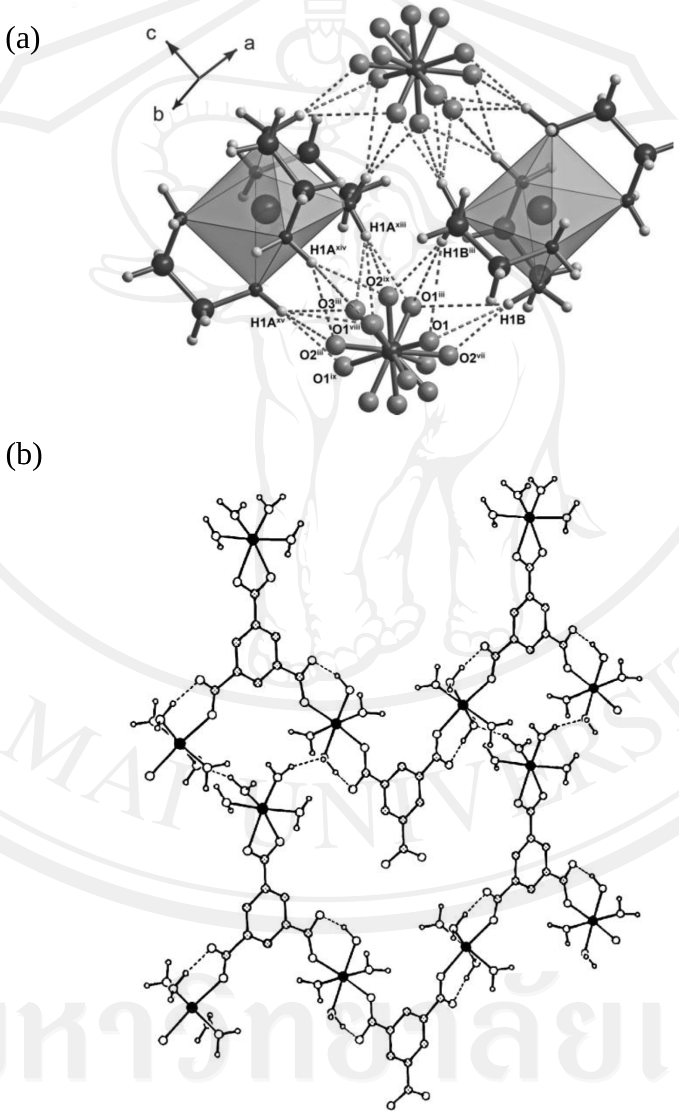

Fig. 1.4 Representation of hydrogen bonding interactions (dotted line) of (a) $[Co^{II}(C_2H_2N_2)_3]SO_4$ [19] and (b) $M_3(BTC)_2\cdot 12H_2O$ [20].

1.1.2 Halogen bond

Halogen bonding interaction has been introduced for describing any non−covalent interactions involving halogens as electron acceptors. It has been defined as a net attractive interaction between an electrophilic region on a halogen atom and another nucleophilic region; R–X···Y−Z [17, 21]. R–X can be a whole molecule or a molecular fragment acting as the halogen bond donor. X is a halogen atom, including fluorine, chlorine, bromine, iodine, and astatine, with an electrophilic region. Y−Z is a halogen acceptor and is typically a mono− or polyatomic anion or a nucleophilic region in a neutral molecule. According to the IUPAC definition [21], some typical features are used as the useful indications for the existence of the halogen bond:

(a) the distance between the donor halogen atom X and the acceptor atom Y tends to be less than a sum of the van der Waals radii of X and Y;

(b) the angle of R−X···Y tends to be linear (180°);

(c) the length of the R−X covalent bond usually increases;

(d) new vibrational modes associated with the formation of the X···Y bond are generated, and changes in the infrared and Raman absorptions of R−X and Y−Z occur;

(e) the X···Y halogen bond usually leads to the characteristic blue shifts in the UV−visible spectrum of the halogen bond donor.

The influences of halogen bonding interactions on the crystal structures of MOMs may be clearly observed in a series of Hg(II) complexes of *N*–(3–halophenyl)–2–pyrazinecarboxamide ligands [22], carrying a different halogen atom in the phenyl meta–position (Fig. 1.5). The replacing of coordinated anions from chloride with bromide and iodide in each series containing the same ligand, the coordination geometry and structural motif of the resulting compounds have been dramatically affected. In addition to MOMs, both hydrogen and halogen bond interactions may involve in the construction of co–crystals of organic ligands [23], as typically shown in Fig. 1.6.

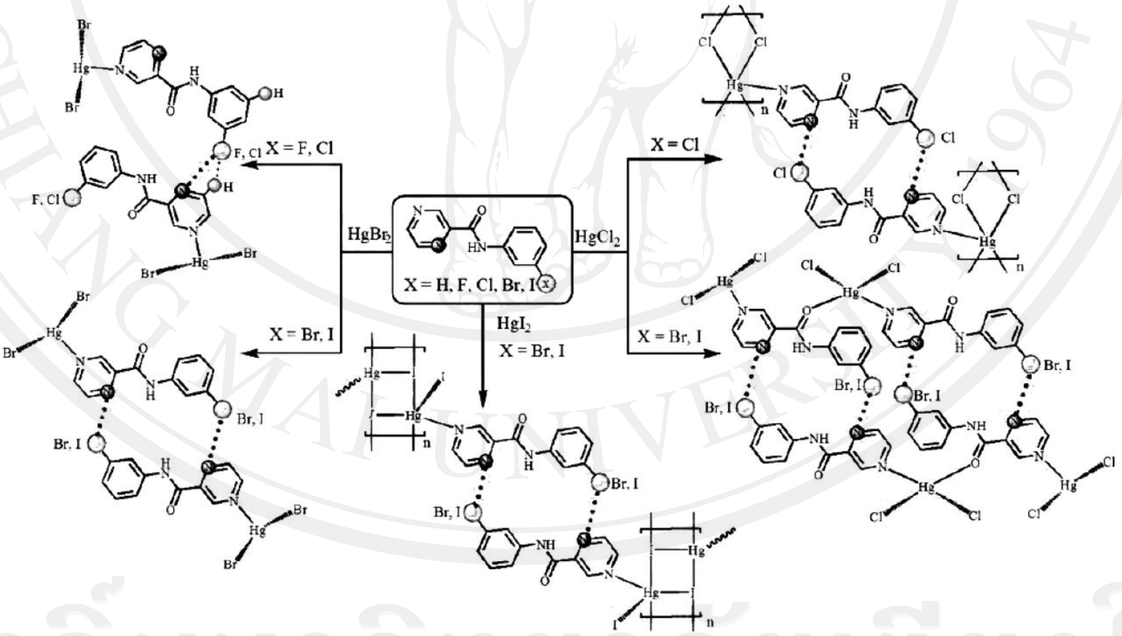

Fig. 1.5 Diagrams showing the presence of halogen bond (dotted line) in a series of Hg(II) complexes [22].

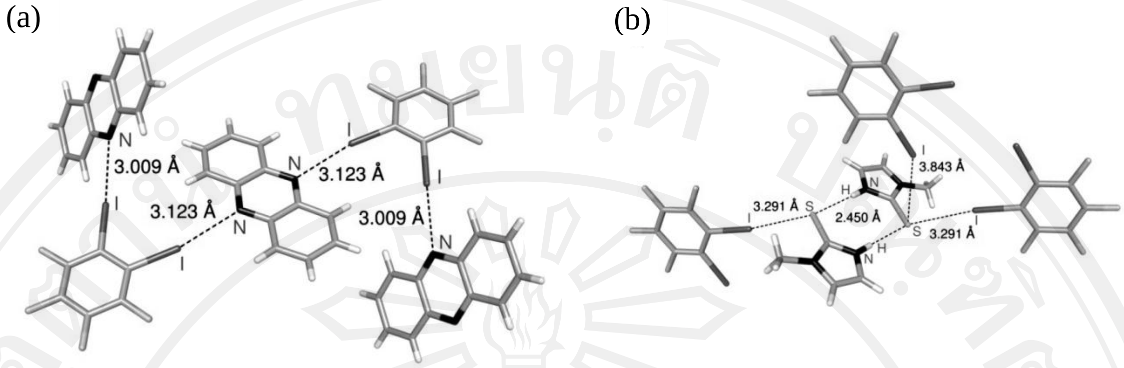

Fig. 1.6 Representation of (a) the presence of halogen bonds in the zigzag chain structure of the co−crystals of (1,2−diiodoterfluorobenzene)·(phenazine) and (b) the halogen and hydrogen bonds in the structure of (2−mercapto−1−methylimidazole)·(1,2−diiodoterfluorobenzene) [23].

1.1.3 Aromatic π−π interactions

Aromatic–aromatic or π−π interactions are as important non−covalent interactions as the hydrogen bonds. They are usually manifested their influence on the variation of the covalent bond distances and angles. The arrangement of π−π interactions may involve perfect or offset face−to−face alignments and edge− or point−to−face or T−shaped arrangements (aromatic C–H···π interaction) [24], as depicted in Fig. 1.7. For face−to−face interactions, the centroid to centroid distance between two aromatic fragments should be in a range of 3.4−3.8 Å. In the case of the offset arrangement, displacement angle should lie between 16 and 40° [24]. The influences of π−π stacking interactions between the aromatic groups can be found vividly in many structures especially those of the porous MOMs, and also in the stacking arrangements of the 2−D layers (Fig. 1.8 and Fig. 1.9);

$[Ni(Phen)_2(H_2O)_2][Ni(PtcH)_2]\cdot 11H_2O$ [25], $[Cu_3(TATB)_2(H_2O)_3]_n$ [26] and $[Ni(1,10\text{–}phen)_2(H_2O)_2](NO_3)_2$ [27], as examples.

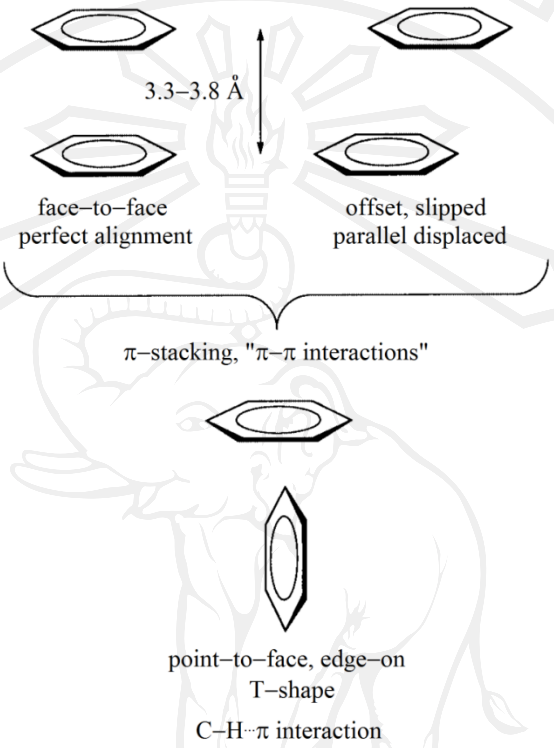

Fig. 1.7 Principal orientations of aromatic–aromatic or π–π interactions [24].

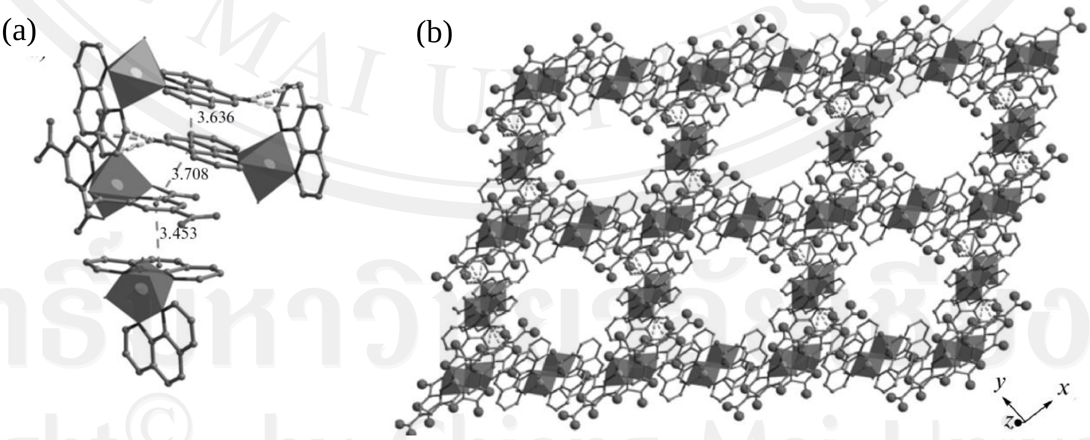

Fig. 1.8 Representation of (a) π–π and CH···π interactions in $[Ni(Phen)_2(H_2O)_2][Ni(PtcH)_2]\cdot 11H_2O$ and (b) the 2–D framework structure with hydrophilic cavities formed by strong π–π and CH···π interactions [25].

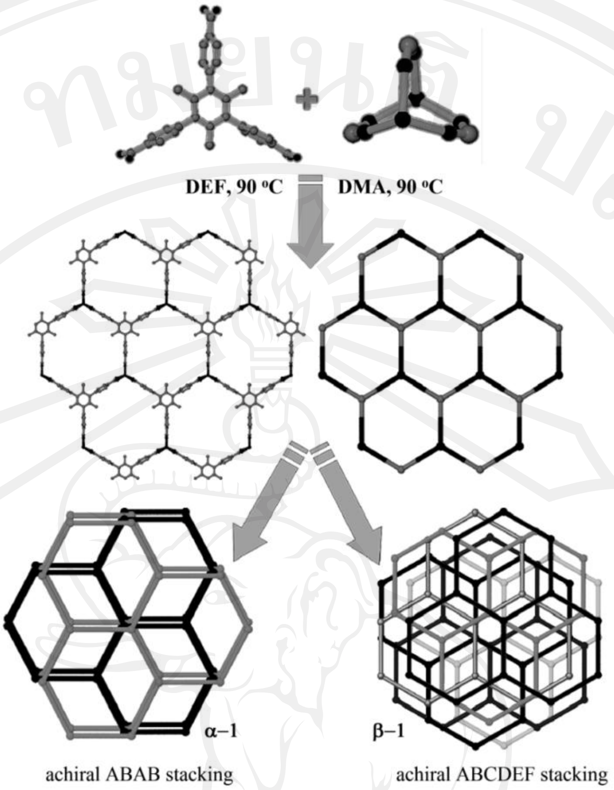

Fig. 1.9 Formation of two isomeric supramolecular architectures. Each isomer consists of 2−D honeycomb layers based on 4,4′,4′′−(2,4,6−trimethylbenzene−1,3,5−triyl)tribenzoic acid (H_3TMTA) and $Zn_2(COO)_3$ SBUs [26].

1.1.4 Aliphatic CH/π interactions

The CH/π interaction can be regarded as the weakest kind of hydrogen bonds occurring between CH−fragments and π−systems, as hydrogen bond donor (soft acid) and acceptor (soft base), respectively. Evidences of the CH/π interaction have been reported in many reviewed articles based on both experimental and theoretical data [28, 29]. Typical details of CH/π interaction between benzene and several saturated hydrocarbons and haloalkanes which support the existence of the interaction are provided in Table 1.2.

Table 1.2 Distance and orientation dependence of the CH/π interactions [28, 29].

Compound	C–H···π distance (Å)	C–H···π plane angle (°)
Cl_3CH	2.53±0.17	157±12
Cl_2CH_2	2.62±0.15	151±13
sp–CH	2.62±0.13	152±13
sp^2–CH	2.73±0.13	148±11
sp^3–CH(CCH_3)	2.75±0.10	148±13
CH_4	2.548	n/a
C_2H_6	2.451	n/a
n–C_3H_8	2.506	n/a
Cyclopropane	2.437	n/a
Isobutane	2.473	n/a
Cyclobutane	2.361	n/a
Cyclopentane	2.402	n/a
Cyclohexane	2.338	n/a
Cycloheptane	2.377	n/a
Cyclooctane	2.376	n/a

Nevertheless, the aliphatic CH/π interactions of MOMs have been less demonstrated. $\{[Zn(L)_2Cl_2]\cdot DMF\cdot CH_3OH\}_n$ is an example that mentioned the existence of the CH/π interactions in MOMs structures [30], as depicted in Fig. 1.10. The other examples that support the existence of this interaction is a series of isostructural $Cu_2(\mu_3\text{–ade})_2(\mu_2\text{–OOC}(CH_2)_nCH_3)_2]_3\cdot xH_2O$ (n from 0 to 5) complexes [31]. It is interesting to note that the free volume of these complexes is related to the length of the aliphatic chain, which is pointing toward the inner portion of the channels (Fig. 1.11).

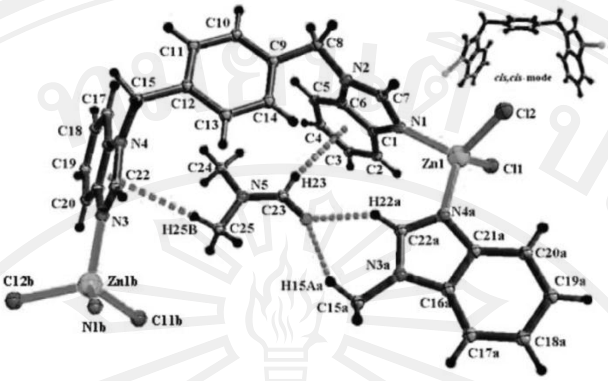

Fig. 1.10 Representation of the existence of the aliphatic CH/π interactions in the crystal structure of $\{[Zn(L)_2Cl_2]\cdot DMF\cdot CH_3OH\}_n$; L is 1,4–bis(benzimidazol–1–ylmethyl)benzene [30].

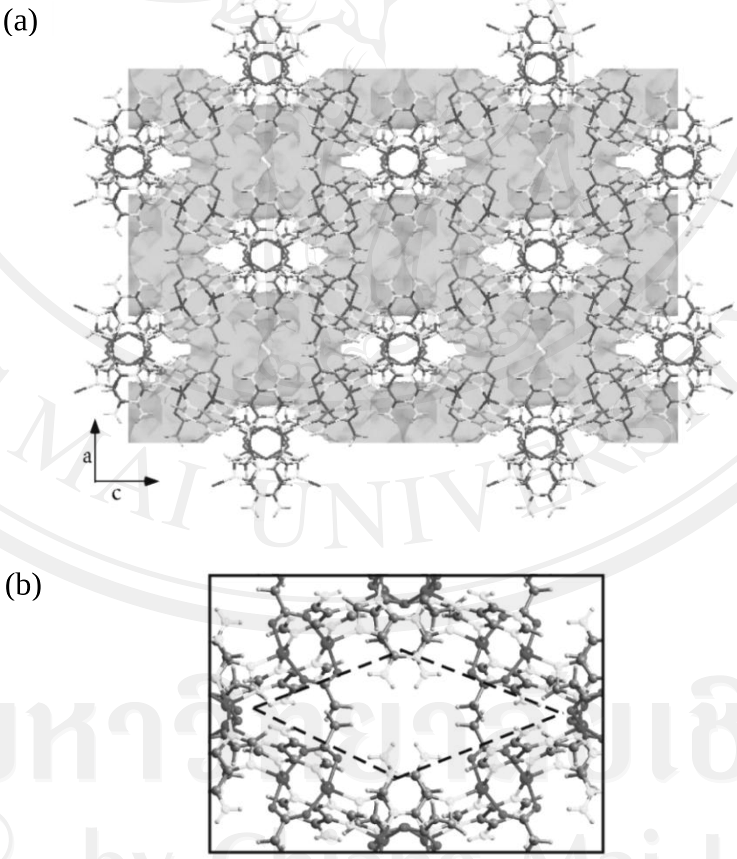

Fig. 1.11 Representation of (a) crystal packing of the acetate compound showing the 3–D network of microchannels (backbone blur) and (b) a cavity with the aliphatic chains pointing toward it [31].

1.2 Synthesis and single crystal growth techniques

Primary goal in the synthesis of new MOMs is to grow single crystals which possess a suitable quality for single crystal X–ray diffraction analysis. There are various methods available for the crystal growth of MOMs such as solvent evaporation, diffusion, reflux, solvo(hydro)thermal, ionothermal and microwave–assisted synthesis [6, 12, 32]. Among these methods, solvent evaporation is the most traditional whereas the solvo(hydro)thermal is the most common. In this research, the vapor diffusion, microwave–assisted hydrothermal and ionothermal methods have been adopted.

1.2.1 Diffusion method

The general principle of diffusion method is to slow the encounter of the different species at contact surface (Fig. 1.12).

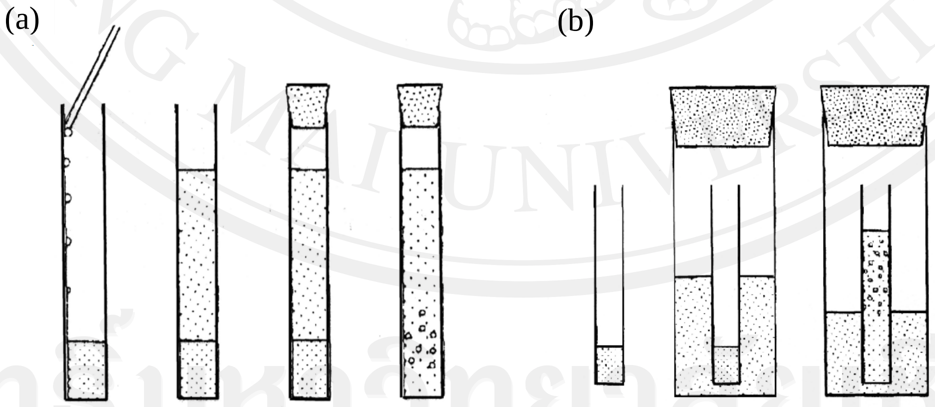

Fig. 1.12 Representation of (a) liquid diffusion and (b) vapor diffusion methods [33].

The slow diffusion of reactants is preferred to yield single crystals of suitable quality for structural determination instead of non– or poly–crystalline products. The diffusion method is commonly performed by allowing two separate solutions of metals and ligands to diffuse slowly into each other leading to a concentration gradient. This is mostly carried out in a sealed tube or vial. Two solutions may be separated by using the physical barriers such as solvents with different densities, buffer layer of pure solvent or gel [6, 33]. The diffusion method can be alternatively performed *via* vapor phase of which volatile reactant is allowed to diffuse into the solution [33].

1.2.2 Solvo(hydro)thermal synthesis

Solvothermal reaction usually refers to either homogeneous or heterogeneous reaction which takes place in a closed system in the presence of a liquid media above room temperature and at pressure greater than 1 atm in order to crystallize solids directly from solution [34, 35]. Typically most of MOMs can be derived under solvothermal conditions using different kinds of organic solvents, and also water (hydrothermal) [3]. The reaction is in general conducted in a sealed autoclave under autogenous pressure at elevated temperatures normally in a range of 120–260 °C [6, 12]. The generally solvothermal reactor composes of a stainless steel body and a removable Teflon liner, as diagrammatically depicted in Fig. 1.13. A spring–loaded closure is fitted with the reactor to help maintaining the pressure in the liner throughout the operation particularly during the cooling process. The rupture disc is required to protect the reactor and the operator from the hazard of unexpected or dangerously high internal pressures. The rupture disc is placed above an inner corrosion disc, which serves as a corrosion barrier to protect the rupture disc from corrosive vapor [34, 36].

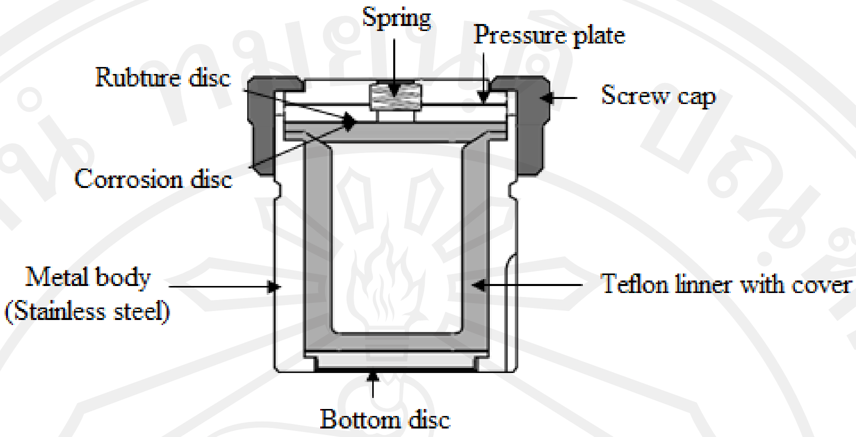

Fig. 1.13 Diagram showing the components of general hydrothermal reactor [36].

The solvo(hydro)thermal technique provides an excellent possibility for the crystal growth. Most importantly, a lowered solvent viscosity is usually reached during the solvothermal treatment. The utilization of low temperature synthesis beneficially allows the formation of metastable compounds and prevents thermal decomposition. Additionally, direct crystallization from the solution provides the ability to control crystal nucleation and growth [36, 37]. However, this technique has some limitations such as a volatility of the organic solvents, a the properties of water in being polar–protic and oxidizing [38, 39].

1.2.3 Microwave–assisted synthesis

Microwave–assisted synthesis generally operates at a frequency of 2.45 GHz corresponding to a wavelength and photon energy of 12.2 cm and 0.0016 eV, respectively [40]. Microwave heating can induce the reaction depending on the ability of materials to absorb microwave energy and convert it into heat. The irradiation of microwave absorbing materials *e.g.* water and other polar solvent with microwave results in an attempt of the dipole molecules to align themselves in the applied field by rotation and energy is then lost in the form of heat (Fig. 1.14). Although the photon energy originated from microwave heating is too low to break chemical bond, the microwave can offer the high ramp rate than that obtained from normal heating. This is because the microwave energy is remotely introduced into the reaction vessels without direct contact between microwave generator and reaction vessel. In addition, the microwave irradiation can be regarded a selective heating because an electric field component of microwave interacts with specific molecules in the reaction medium [40, 41].

Fig. 1.14 Dipolar molecules trying to align with an oscillating electric field of microwave component [41].

In the synthesis of MOMs *e.g.* IRMOF2 [42], IRMOF3 [42], $[Co(H_2O)_4(4,4'-bipyridine)](4,4'-bipyridineH_2)\cdot 2(SO_4)\cdot 2H_2O$ [43.] and $[Ni(2,2'-bipyridine)(H_2O)_3(NO_3)](NO_3)$ [44], microwave heating dramatically reduces the reaction time from hours or days to seconds or minutes. However, microwave–assisted synthesis is so far not common method for the synthesis and crystal growth because the rapid ramping can easily induce defects to the crystal quality [4, 6].

1.2.4 Ionothermal synthesis

Recently, ionothermal synthesis involving with the use of ionic liquids (ILs) as an alternative solvent or reaction media, has emerged as one of potential methods for the exploratory of new MOMs [39, 45]; $(BMIm)_2[Cd_3(BDC)_3Br_2]$ [46], $(EMIm)_2[Ni_3(TMA)_2(OAc)_2]$ [47], $(EMIm)[Co_2(TMA)_4H_7(2,2'\text{–}bpy)_2]$ [48] and $[Zn_3(BTC)_2(H_2O)_2]\cdot 2H_2O$ [49], for instances. Room temperature ILs are salts of organic cations and mostly inorganic anions that are liquid preferably at room temperature or at temperatures less than 100 °C [39, 45]. Typical cations and anions used as ionic liquids are depicted in Fig. 1.15.

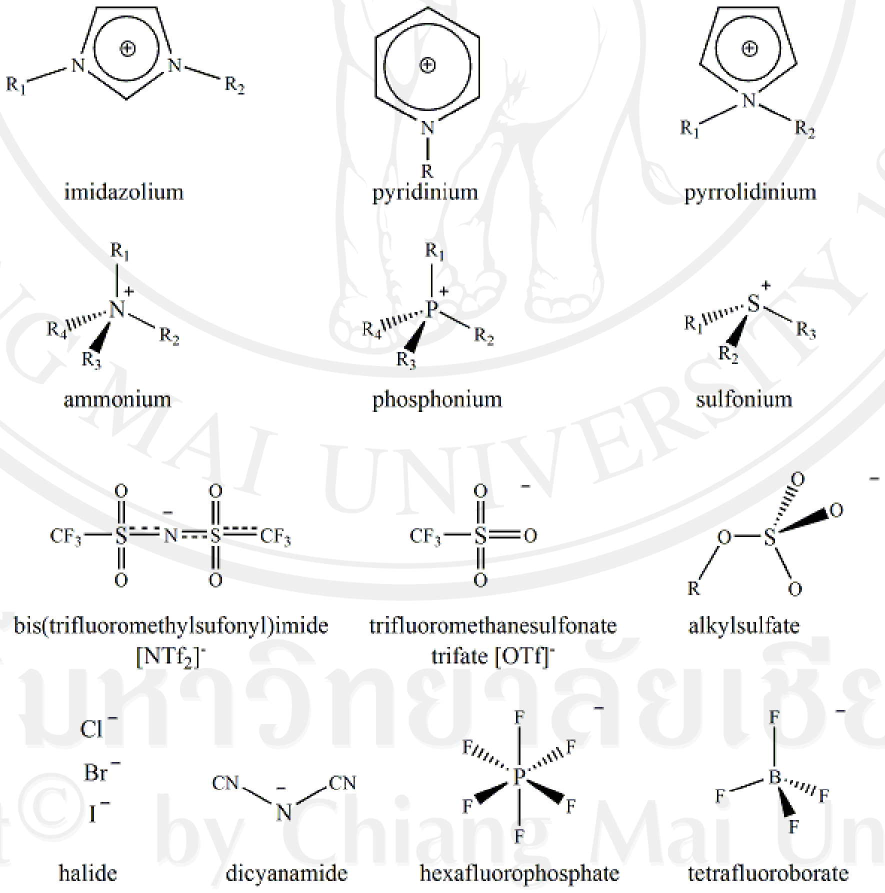

Fig. 1.15 Some typical cations and anions commonly used as the component of ILs [51, 52].

There are several characteristics of ILs that can be very useful for the synthesisof MOMs [39, 45]. Firstly, ILs can be relatively polar solvents and therefore reasonably good solvents for inorganic precursors. Secondly, ILs have very low vapor pressure impling a very low volatility and flammability which make them environmentally benign as well as suitable for high temperature reactions. In addition, the high ionic conductivity and polarizability of ILs make them the excellent microwave−absorbing agents that can be applied in microwave synthesis. Thirdly, ILs can be regarded as “designer solvents” as their properties can be tuned for a specific application by varying the combinations of cations and anions. Lastly, ILs do not only serve as solvent or reaction media in the ionothermal synthesis but may also function as templates, charge compensating groups and coordinating ligands [39, 45−50].

1.3 Polycarboxylate and amino acids as ligands

Among numerous organic ligands, the polycarboxylate ligands have been proven to be one of the most effective ligands due to a great variety of coordination modes. The carboxylate group can coordinate with metal centers through monodentate, bidentate, chelating or bridging fashions, as shown in Fig. 1.16 [53−56]. The notations for ligating atoms in coordination complexes are described in Appendix A. Most of porous structures, which are very useful in gas storage, gas separation and catalysis, were usually constructed from metals and polycarboxylate ligands. The difference in flexibility of ligand evidently show influences on the particular structures and properties [57]. The rigid ligands; on the other hand, can provide more rigid structures and better structural prediction. For example, reactions of Zn^{II} ions with 1,4−benzenedicarboxylic acid (H_2BDC) which has rigid structure led to a design and synthesis of a series of isorecticular 3–D porous frameworks reported by O.M. Yaghi *et al.* (Fig. 1.17) [56, 58].

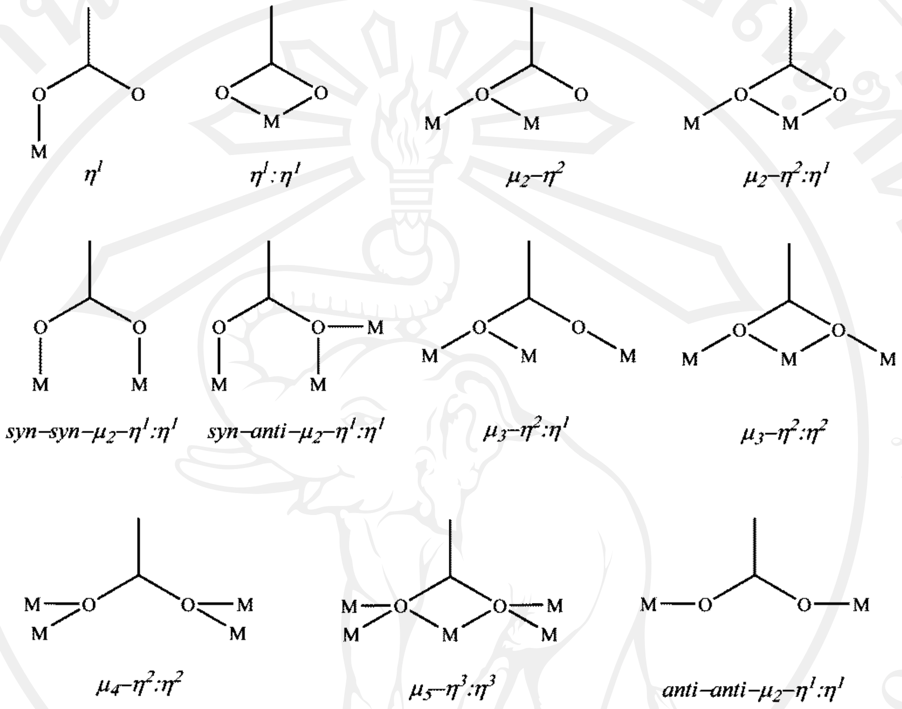

Fig. 1.16 Diagrams showing different coordination modes of carboxylate groups [54].

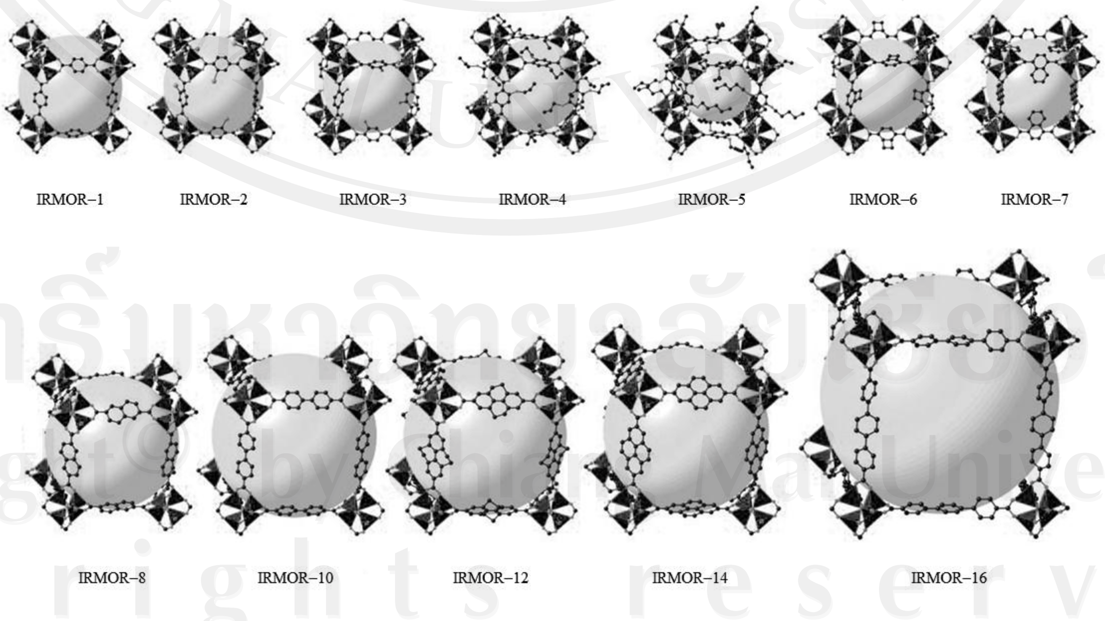

Fig. 1.17 A large series of isoreticular IRMOFs [46].

The flexible ligands however express versatile conformations depending on geometric requirements of different metal ions, and therefore offer a great variety of interesting structures and properties. The 1,3,5–triazine–2,4,6–triaminehexaacetic acid (TTHA) which has flexible arms, shows different coordination modes (Fig. 1.18) and conformation with different metals *e.g.* $\{Na_2[Co_3(H_2TTHA)_2(H_2O)_{12}](H_2O)_2\}\cdot 4H_2O$, $\{Na[Cu_4(H_2TTHA)(HTTHA)(H_2O)_8](H_2O)_3\}\cdot 5H_2O$, $[Cd_3(TTHA)(H_2O)_4]$ and $[Ca_5(HTTHA)_2(H_2O)_8]$ [59]. It may be noted that the TTHA ligand does not only provide rich structure variation because of its structural flexibility but also the excellent fluorescent emission due to its triazine–core [59–61].

Amino acid containing amino and carboxylate functional residues are the other interesting biological ligands. They have been extensively investigated in the construction of chiral MOMs, which exhibit potential applications in chiral catalysis and separation as well as in biomedical industry [62, 63]; $\{Cu(D\text{–}\alpha\text{–}PhGly)_2\}$ [64], $[Cu(L\text{–}NH_2\text{–}Phe)(bpy)]NO_3\cdot H_2O$ [65], $[Cu(L\text{–}Tyr)(phen)]ClO_4\cdot 2.5H_2O$ [65], $[Cu(L\text{–}Phe)(phen)]Cl\cdot 3H_2O$ [65], $[Cu(L\text{–}Phe)(bpy)]ClO_4\cdot H_2O$ [65] and $[Zn(HPO_3)(C_{11}N_2O_2H_{12})]$ [62]. Among the twenty–four amino acids, the aromatic amino acids including phenylalanine (Phe), tyrosine (Tyr) and tryptophan (Trp), are good candidates due to not only their feasible coordination ability but also their biological activities *e.g.* antibacterial, antiviral and antifungal; $[Cu(Tyr)_2]_n$ [66], $[Cu_2(Tyr)_2(4,4'\text{–}bipy)\cdot 2H_2O]\cdot 2ClO_4\}_n$ [66] $[Cu(bpy)(I_2TyrOH)(NO_3)]\cdot CH_3OH$ [67], $\{[Zn(Tyr)_2(H_2O)]H_2O\}_n$ [66].

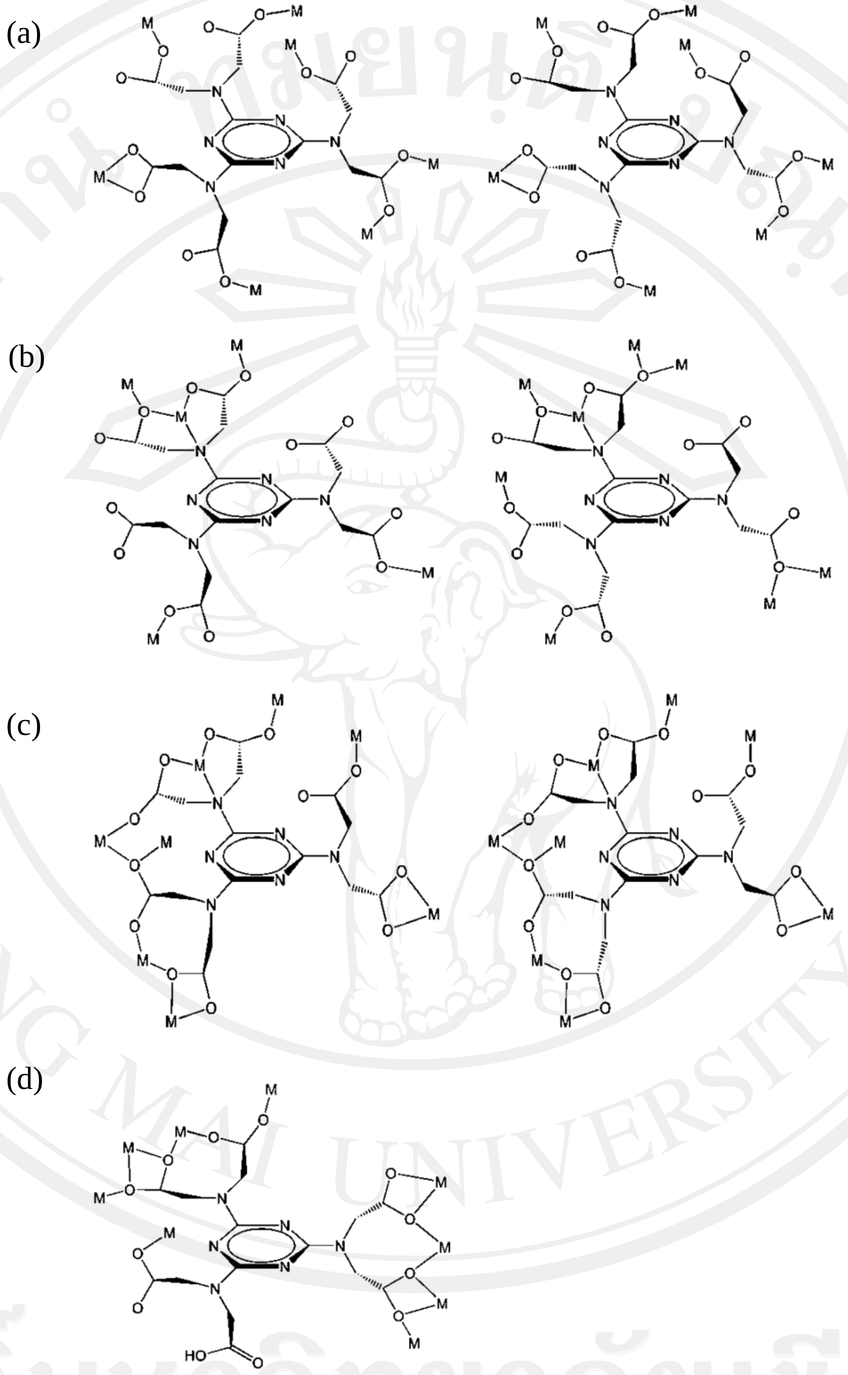

Fig. 1.18 Coordination modes of TTHA in (a) $\{Na_2[Co_3(H_2TTHA)_2(H_2O)_{12}](H_2O)_2\}\cdot 4H_2O$, (b) $\{Na[Cu_4(H_2TTHA)(HTTHA)(H_2O)_8](H_2O)_3\}\cdot 5H_2O$, (c) $[Cd_3(TTHA)(H_2O)_4]$ and (d) $[Ca_5(HTTHA)_2(H_2O)_8]$ [59].

In this research, we have synthesized and determined the crystal structures of a new polymorph of 1,3,5–triazine–2,4,6–triaminehexaacetic acid (TTHA) ligand and five new structures of MOMs, which are constructed from the first–row transition metals, *i.e.* Ni, Co and Zn, and either the polycarboxylate or amino acid ligands including *L*–4–hydroxyphenylalanine (*L*–tyrosine), 4–pyridinecarboxylic acid (isonicotinic acid) and 1,4–benzenedicarboxylic acid (terephthalic acid). These structures are reported in the following Chapters as listed:

Chapter 2: $C_{15}H_{18}O_{12}N_6$ (**TTHA–II**)

Chapter 3: $[Ni_3(C_9H_{11}NO_3)_6(OCH_3)]\cdot 4CH_3OH$ (**I**)

Chapter 4: $[Co(C_9H_{10}NO_3)(C_6H_4NO_2)(H_2O)_2]$ (**II**)
$[Ni(C_9H_{10}NO_3)(C_6H_4NO_2)(H_2O)_2]$ (**III**)

Chapter 5: $(C_6H_{11}N_2)_2[Zn_3(C_8H_4O_4)_3Cl_2]$ (**IV**)
$(C_8H_{15}N_2)_2[Zn_3(C_8H_4O_4)_3Cl_2]$ (**V**).

1.4 Research objectives

1.4.1 To synthesize and grow single crystals of new MOMs based on the first–row transition metals and either polycarboxylate or amino acid ligands.

1.4.2 To investigate the feasibility in using ionic liquids as alternative solvents in the synthesis of new MOMs using polycarboxylate ligands.

1.4.3 To establish the understanding on the influences of supramolecular interactions on regulating the assembly of inorganic and organic components in the fabricated frameworks.

1.4.4 To study physical and chemical properties, *e.g.* thermal stability and luminescence properties, of the new complexes, and to rationalize the corresponding structure–properties relations.

1.5 Research plan

Research Activities	**First year**				**Second year**				**Third year**			
	1	2	3	4	1	2	3	4	1	2	3	4
1. Review literatures.	■	■	■	■	■	■	■	■	■	■	■	■
2. Synthesize and grow single crystals of new MOMs, using first–row transition metals hybridized with carboxylate and amino acid ligands.	■	■	■	■	■	■	■	■	■	■		
3. Characterize single crystal structures mainly by X–ray diffraction techniques (powder and single crystal), and also other spectroscopic techniques, *e.g.* FT–IR, Raman, UV–Visible and CHNS/O.	■	■	■	■	■	■	■	■	■	■	■	
4. Investigate physical and chemical properties, *e.g.* thermal stability and luminescence properties of new MOMs, using thermogravimetric analyzer and luminescence spectroscopy.			■	■	■	■	■	■	■	■	■	
5. Prepare articles for international publications and international conferences/workshops.			■	■	■	■	■	■	■	■	■	■
6. Write up the thesis.											■	■

REFERENCES

1. S.R. Batten, S.M. Neville, D.R. Turner, Coordination Polymers Design, Analysis and Application, The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK, 2009.
2. M. Schröder, Functional Metal−Organic Frameworks: Gas Storage, Separation and Catalysis, Springer Heidelberg Dordrecht London New York, 2010.
3. R.J. Kuppler, D.J. Timmons, Q.–R. Fang, J.–R. Li, T.A. Makala, M.D. Young, D. Yuan, D. Zhao,W. Zhuang, H.–C. Zhoua, Coord. Chem. Rev. 253 (2009) 3042.
4. J.L.C. Rowsell, O.M. Yaghi, Micropor. Mesopor. Mat. 73 (2004) 3.
5. S. Natarajan, P. Mahata, Chem. Soc. Rev. 38 (2009) 2304.
6. S. Qiu, G. Zhu, Coordin. Chem. Rev. 253 (2009) 2891.
7. A.K. Cheetham, C.N.R. Rao, R.K. Feller, Chem. Commun. (2006) 4780.
8. J.J. Perry IV, J.A. Perman, M.J. Zaworotko, Chem. Soc. Rev. 38 (2009) 1400.
9. G.A. Lawrance, Introduction to Coordination Chemistry, John Wiley & Sons Ltd, 2010.
10. K. Biradha, C.−Y. Su, J.J. Vittal, Cryst. Growth Des. 11 (2011) 875.
11. J.W. Steed, J.L. Atwood, Supramolecular Chemistry, John Wiley & Sons, Ltd, 2009.
12. A.Y. Robin, K.M. Fromm, Coord. Chem. Rev. 250 (2006) 2127.
13. G.R. Desiraju, J. Mol. Struct. 656 (2003) 5.
14. D. Braga, Chem. Commun. (2003) 2751.
15. Z. Lin, M.–L. Tong, Coord. Chem. Rev. 255 (2011) 421.

16. G.R. Desiraju, J.J. Vittal, Crystal Engineering: A Textbook, World Scientific Publishing, Singapore, 2011.
17. T. Steiner, Angew. Chem. Int. Ed. 41 (2002) 48.
18. B.–B. Ding, Y.–Q. Weng, Z.–W. Mao, C.–K. Lam, X.–M. Chen, B.–H. Ye, Inorg. Chem. 44 (2005) 8836.
19. B. Yotnoi, A. Seeharaj, Y. Chimupala, A. Rujiwatra, Acta Cryst. E66 (2010) m628.
20. O.M. Yaghi, H. Li, T.L. Groy, J. Am. Chem. Soc. 118 (1996) 9096.
21. G.R. Desiraju, P.S. Ho, L. Kloo, A.C. Legon, R. Marquardt, P. Metrangolo, P.A. Politzer, G. Resnati, K. Rissanen, Definition of the Halogen Bond, Recommendation submitted by the IUPAC task group (2009−032−1−100).
22. H.R. Khavasi, A.A. Tehrani, Inorg. Chem. 52 (2013) 2891.
23. X. Ding, M. Tuikka, M. Haukka, Recent Advances in Crystallography, 10.5772/48592.
24. C. Janiak, J. Chem. Soc. Dalton Trans. (2000) 3885.
25. K.H. Wanga, M.C. Zhub, L. Liub, E.J. Gaob, D.Y. Houa, G. Xina, T.C. Lia, Russ. J. Coord. Chem.$^+$ 38 (2012) 29.
26. X. Zhao, H. He, F. Dai, D. Sun, Y. Ke, Inorg. Chem. 49 (2010) 8650.
27. T.J. Prior, A. Rujiwatra, Y. Chimupala, Crystals 1 (2011) 178.
28. M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyamad, H. Suezawa, Cryst. Eng. Comm. 11 (2009) 1757.
29. M. Nishio, Phys. Chem. Chem. Phys. 13 (2011) 13873.
30. J.–Q. Chen, Y.–P. Cai, H.–C. Fang, Z.–Y. Zhou, X.–L. Zhan, G. Zhao, Z. Zhang, Cryst. Growth Des. 9 (2009) 1605.

31. S.P. Yáñnez, G. Beobide, O. Castillo, J. Cepeda, A. Luque, A.T. Aguayo, P. Román, Inorg. Chem. 50 (2011) 5330.
32. U. Schubert, N. Hüsing, Synthesis of Inorganic Materials, Wiley–VCH, Weinheim, 2000.
33. P.G. Jones, Chem. Brit. 7 (1981) 222.
34. K. Byrappa, M. Yoshimura, Handbook of Hydrothermal Technology: A Technology for Crystal Growth and Materials Processing, Park Ridge, New Jersey, USA, 2000.
35. M. Yoshimura, K. Byrappa, J. Mater. Sci. 43 (2008) 2085.
36. R.A. Laudise, Chem. Eng. News (1987) 30.
37. R.E. Riman, W.L. Suchanek, M.M. Lencka, Ann. Chim. Sci. Mat. 27 (2002) 15.
38. R.D. Rogers, K.R. Seddon, Science 302 (2003) 792.
39. E.R. Parnham, R.E. Morris, Acc. Chem. Res. 40 (2007) 1005.
40. C.O. Kappe, Angew. Chem. Int. Ed. 43 (2004) 6250.
41. P. Lindström, J. Tierney, B. Watheym, J. Westman, P. Lindström, J. Tierney, B. Watheym, J. Westman, Tetrahedral 57 (2001) 9225.
42. Z. Ni, R.I. Masel, J. Am. Chem. Soc. 128 (2006) 12394.
43. T.J. Prior, B. Yotnoi, A. Rujiwatra, Polyhedron 30 (2011) 259.
44. A. Rjiwatra, S. Yimklan, T.J. Prior, Polyhedron 31 (2012) 345.
45. R.E. Morris, Chem. Commun. (2009) 2990.
46. J.–H. Liao, W.–C. Huang, Inorg. Chem. Commun. 9 (2006) 1227.
47. Z. Lin, D.S. Wragg, R.E. Morris, Chem. Commun. (2006) 2021.
48. Z. Lin, D.S. Wragg, J.E. Warren, R.E. Morris, J. Am. Chem. Soc. 129 (2007) 10334.

49. L. Xu, E.–Y. Choi, Y.–U. Kwon, Inorg. Chem. 46 (2007) 10670.
50. J. Zhang, S. Chen, X. Bu, Angew. Chem. Int. Ed. 47 (2008) 5434.
51. P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
52. J.P. Hallett, T. Welton, Chem. Rev. 111 (2011) 3508.
53. C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466.
54. H. Li, B. Zhao, R. Ding, Y. Jia, H. Hou, Y. Fan, Cryst. Growth Des. 12 (2012) 4170.
55. M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O’Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.
56. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O.M. Yaghi, Science 295 (2002) 469.
57. D. Zhao, D.J. Timmons, D. Yuan, H.–C. Zhou, Accounts Chem. Res. 44 (2011) 123.
58. H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature 402 (1999) 276.
59. Q. Zhu, T. Sheng, R. Fu, S. Hu, C. Shen, X. Ma, X. Wu, Cryst. Eng. Comm. 13 (2011) 2096.
60. S.N.G. Acharya, R.S. Gopalan, G.U. Kulkarni, K. Venkatesana, S. Bhattacharya, Chem. Commun. (2000) 1351.
61. Q. Zhu,T. Sheng, R. Fu, S. Hu, J. Chen, S. Xiang, C. Shen, X. Wu, Cryst. Growth Des. 9 (2009) 5128.
62. E. Farkas, I. Sóvágó, Amino Acids, Pept. Proteins 27 (2012) 66.
63. A.C. McKinlay, R.E. Morris, P. Horcajada, G. Férey, R. Gref, P. Couvreur, C. Serre, Angew. Chem. Int. Ed. 49 (2010) 6260.

64. J.K. Maclaren, C. Janiak, Inorg. Chim. Acta 389 (2012) 183.
65. T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi, Inorg. Chem. 36 (1997) 576.
66. J. Weng, M. Hong, Q. Shi, R. Cao, A.S.C. Chan, Eur. J. Inorg. Chem. (2002) 2553.
67. F. Zhang, A. Odani, H. Masuda, O. Yamauchi, Inorg. Chem. 35 (1996) 7148.
68. A. Wojciechowska, M. Daszkiewicz, A. Bieńko, Polyhedron 28 (2009) 1481.