

CHAPTER 1

INTRODUCTION

To overcome technological barrier and to fulfill an unceasing demands of human being in achieving better life quality in a better world, the concept of smart and green materials and/or technologies have become solemn [1–5]. The idea of inorganic – organic hybrid framework compounds, literally defining the framework compounds composing of both inorganic and organic components in the same framework structure and at molecular scale [6], has correspondingly gained importance. The basic concept of the inorganic – organic hybrid framework compounds is to merge the corresponding properties and functions of both components within single structure. The different range of interactions between the inorganic and the organic counterparts and other parameters, such as metal coordination preference and ligand structural geometry, may result in novel chemistry which is not known for classical framework solids [7]. In particular, when structural design strategy is adopted [8, 9], a huge range of novel structures with potentially useful properties, for example, porosity [10], chirality [11], selective sorption [12], gas storage [13–15], catalysis [16], non-linear optical properties [17], and guest-responsive magnetism [18], can be generated. As shown in Figure 1.1, an increase in numbers of this type of compounds reported during 1990 to 2011 certifies the growth of their importance. In reference to the framework architecture and

interactions, it should be noted that various terminologies such as coordination polymers, metal–organic frameworks (MOFs), [19, 9], metal-organic coordination compounds (MOCCs) [20, 21] have been confusingly employed in addition to the inorganic–organic hybrid terminology [22, 23].

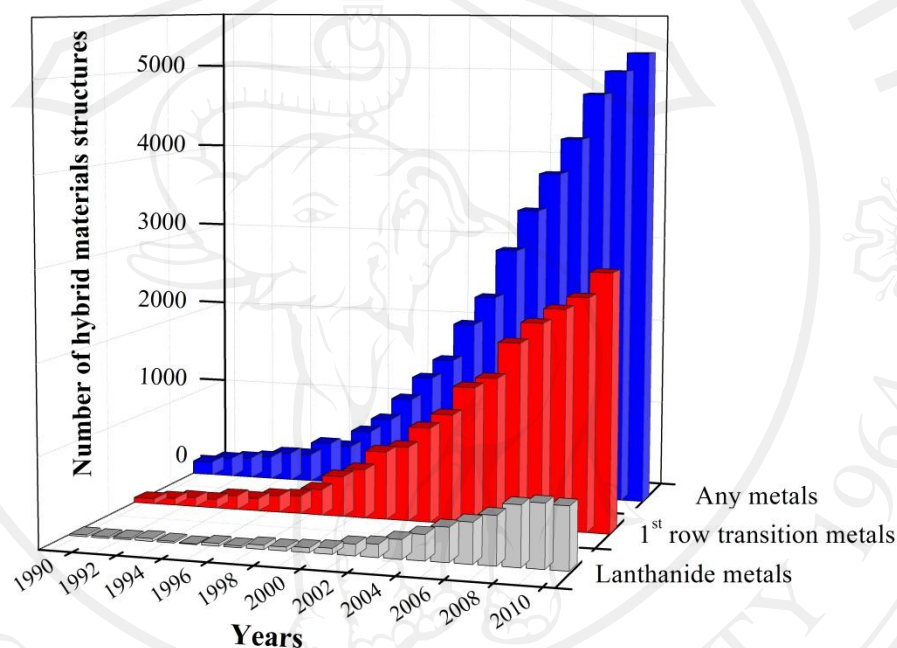


Figure 1.1 The outgrowth in numbers of inorganic–organic hybrid materials reported in Cambridge Structure Database during 1990 to 2011 [24].

One of the utmost important key factors determining a successful fabrication of such frameworks is the understanding on how the inter– and intra–components interactions regulate the framework architectures, and the application of such understanding in building new frameworks with targeted structures and/or functions [25, 26]. The basic technique used for directing the formation of these frameworks is to utilize an appropriate structure directing agent or a template. One of the most

widely utilized organic templates are polyamines. Molecular structure and charge of the templates are all important in determining the nature of the frameworks obtained [27, 28].

1.1 Definition and classification of inorganic–organic hybrid materials

Despite the controversy in terminologies defining these framework materials, there have been attempts in distinguishing difference between these terms. A. K. Cheetam *et. al.* [5], for instance, divided the hybrid framework compounds into two categories. The first group includes coordination polymers (CPs) or metal – organic framework (MOFs), defined as the extended arrays of isolated metal atoms or clusters (M) that are linked by polyfunctional organic ligand (L) and are based upon M–L–M connectivity. The other group is called extended inorganic hybrids specifying the structures based upon oxygen bridges which often contain infinite M–O–M arrays as part of the structures. The extended inorganic hybrids also include a larger class of extended M–X–M arrays where X represents other atoms such as Cl, N or S, or inorganic groups such as phosphate. In addition to such classification, relationship between the dimensionalities of the inorganic and organic components and those of the ultimate frameworks, as shown in Figure 1.2, was proposed.

Figure 1.2 Proposed classification of hybrid materials, according to the dimensionality of the ultimate structures with respect to the organic connectivity between metal centers (O^n) and extended inorganic connectivity (I^n) [5].

		Dimensionality of inorganic connectivity, I^n ($n = 0-3$)			
Metal-organic-metal connectivity, O^n ($n = 0-3$)		0	1	2	3
	0	Molecular complexes I^0O^0	Hybrid inorg. Chains I^1O^0	Hybrid inorg. layers I^2O^0	3-D inorg. hybrids I^3O^0
	1	Chain coordination polymers I^0O^1	Mixed inorg. – organic layers I^1O^1	Mixed inorg. – organic 3-D framework I^2O^1	—
	2	Layered coordination polymers I^0O^2	Mixed inorg. – organic 3-D framework I^1O^2	—	—
	3	3-D coordination polymers I^0O^3	—	—	—

The proposed relationship based on dimensionalities of the components and the fabricated frameworks does favor the generally adopted strategies in designing the framework structure, so-called the crystal engineering concept. Here, the desired framework structure is segmented into simpler repeating building blocks which can then be re-organized back [6].

Figure 1.3 illustrates typical examples of the fabrication using various types of building blocks and connectivities. According to the report made in “China-India-Singapore Symposium on Crystal Engineering” in 2011, three different approaches of crystal engineering have been developed recently [29]:

- direct linking of building blocks (BBs) with organic “struts” using coordination bonds
- 0D $\rightarrow$ 3D, 1D $\rightarrow$ 3D, and 2D $\rightarrow$ 3D dimensional increase *via* weak noncovalent interactions such as hydrogen bonds
- 1D $\rightarrow$ 3D and 2D $\rightarrow$ 3D dimensional increase *via* interpenetrate or catenation.

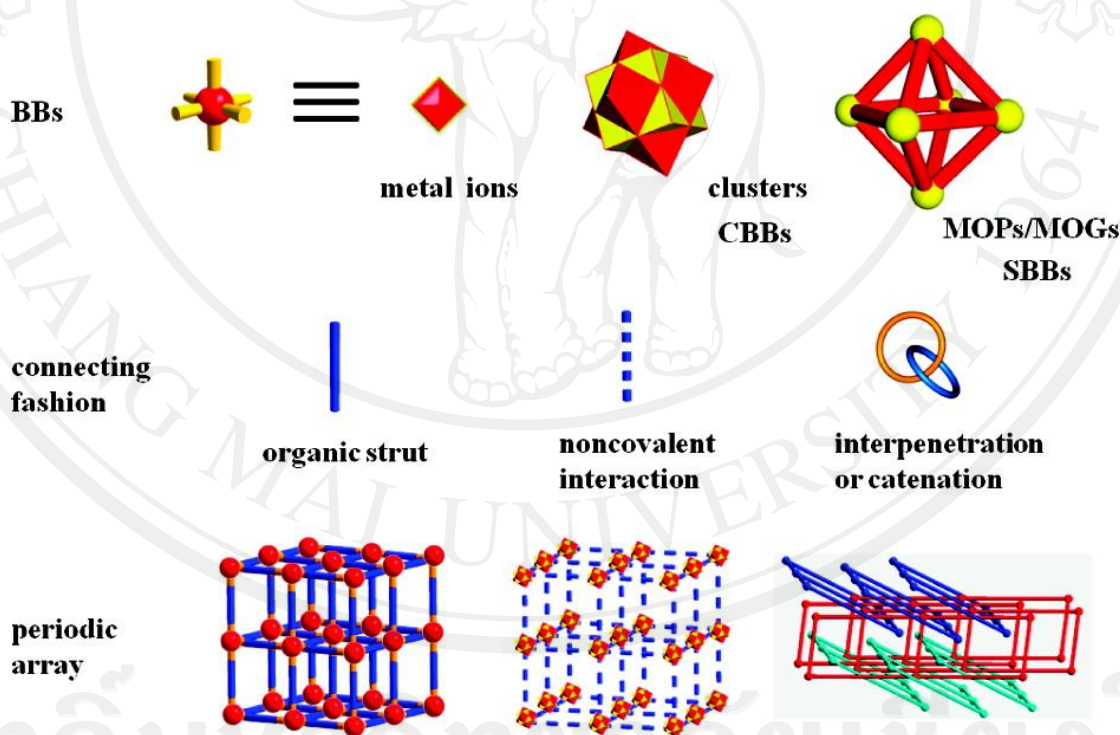


Figure 1.3 Illustration of design strategies in inorganic crystal engineering by means of different building blocks and dimensional increasing fashions.

1.2 Synthesis and single crystal growth of inorganic–organic hybrid compounds

The challenge in the synthesis of inorganic–organic hybrid materials is to obtain single crystals of suitable quality for single crystal x–ray diffraction analysis. At present, various methods are available: conventional hydrothermal, microwave-assisted hydrothermal, layer diffusion, reflux, sol–gel *etc.* In this research only the conventional and microwave–assisted hydrothermal routes were adopted.

Hydrothermal synthesis is one widely exploited route for crystal growth of inorganic–organic hybrid materials, and this typically takes days or weeks to generate crystals of an appropriate size for diffraction experiments. The prime mechanism in the hydrothermal reaction is the self-assembly of products from soluble precursors. The reactions are held in a closed space (autoclave) under either applied or autogenous pressure. Under these conditions the reduced viscosity of water enhances the diffusion process and thus the extraction of solids and crystal growth from solution is favored. This crystallization technique is a non-equilibrium synthesis and may lead to metastable products.

Despite the great success of microwave heating in organic synthesis [30], the application of this technique to inorganic materials is poorly developed. Recently, microwave–assisted hydrothermal chemistry has been utilized in the crystal growth of inorganic–organic hybrid materials [31, 32]. The microwave heating helps to shorten the reaction time from days or weeks to minutes [33].

1.3 Overview on first-row transition metal–organic hybrid materials

It was only in the last few decades that scientists and technologists have realized the potential of the hybrid framework compounds in answering the demand for advanced technologies and therefore to comfort human beings. As statistically illustrated in Figure 1.4, numbers of articles published on the first-row metal–organic hybrid materials have increased unceasingly, particularly in the late 20th century. Among the reported structures, the organic molecules involved in the synthesis contain astonishingly either O– or N– donating moieties. In regard to the first-row transition metals, the predominance of the N–ligands is apparent. This is particularly true for the late transition metals. Among the N–donor ligands, the diamine–derivative compounds of *trans*-geometry, *e.g.* 1,2–diaminoethane, 1,3–diaminopropane, 1,4–diaminobutane, 1,4–diazabicyclo[2.2.2]octane (DABCO) and 4,4′–bipyridine (4,4′–bipy) are $[V_2^{IV}O_8V_2^VO_2](C_2H_{10}N_2)$, $[V_2^{IV}O_8V_2^VO_2](C_3H_{12}N_2)$, $[V_4^{IV}O_{10}V_2^VO_4](C_4H_{14}N_2)$, $[V_4^{IV}O_{10}V_2^VO_4](C_5H_{16}N_2)$ and $Co_2(4,4′-bipy)_2(V_4O_{12})$ [34, 35]. This may be due to the ready availability of functions of the organic molecules and the coordination chemistry of the transition metals synergistically governing the registration of the framework topologies [36].

Among the first-row transition metals, cobalt, which is a hard ferromagnetic silver-white element with high Curie temperature (>1100°C) and common oxidation states of divalence (Co^{II}) and trivalence (Co^{III}) [37], provides very fascinating coordination chemistry and various physical properties. According to the survey of the Co–polyamine hybrid structures deposited to the Cambridge Structure Database, 712 structures were reported during 1957–present [24]. If these structures are to be

classified according to types of the anions present within the same framework (Figure 1.5), the hybrid frameworks of Co/Vanadate and Co/Sulfate are of our interest, and they will be detailed in Chapter 2 and Chapter 3, respectively. For the Co/Vanadate system, the versatile oxidation states (V^{II} to V^V) and coordination geometries of the vanadium is the additional factor providing the complexity of the yielded structures [38, 39] which can exhibit various dimensionalities; $[\text{Co}(\text{phen})_2]_2\text{V}_4\text{O}_{12} \cdot \text{H}_2\text{O}$ (OD) [40], $\text{Co}(\text{dien})_2(\text{VO}_3)_3 \cdot (\text{H}_2\text{O})$ (1D) [41], $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$ (2D) [42], $\text{Co}(\text{pz})(\text{VO}_3)_2$, $\text{Co}_2(2\text{-pzc})(\text{H}_2\text{O})(\text{VO}_3)_3$ (3D) [35] and $[\text{CoV}_2\text{O}_6(4,4'\text{-bipy})]$ (3D) [43], for instance.

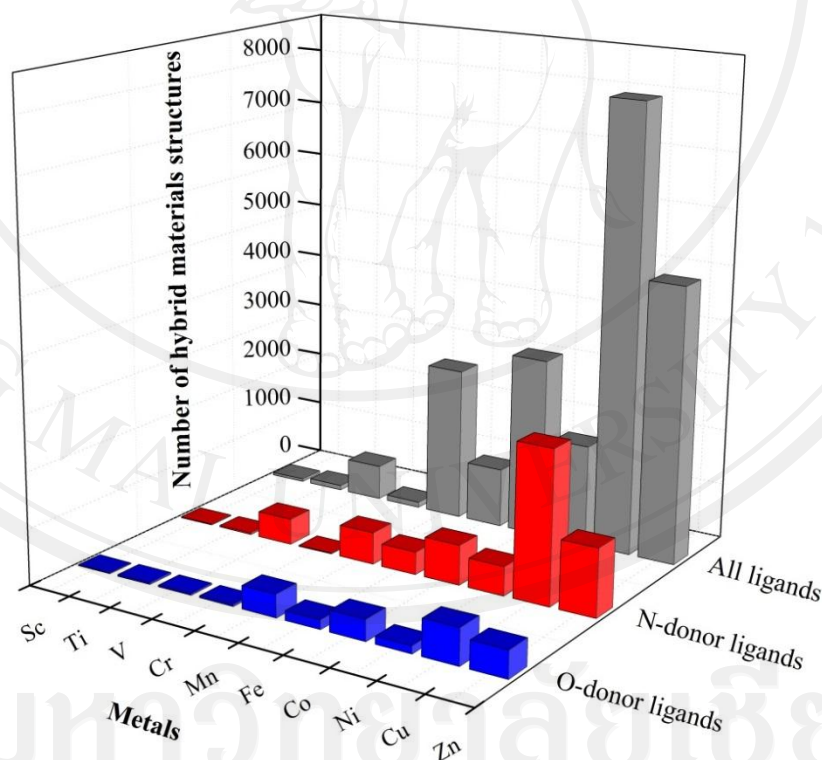


Figure 1.4 Numbers of the first-row transition metals–organic hybrid frameworks deposited in Cambridge Structure Database, during 1957 – May, 2012 [24].

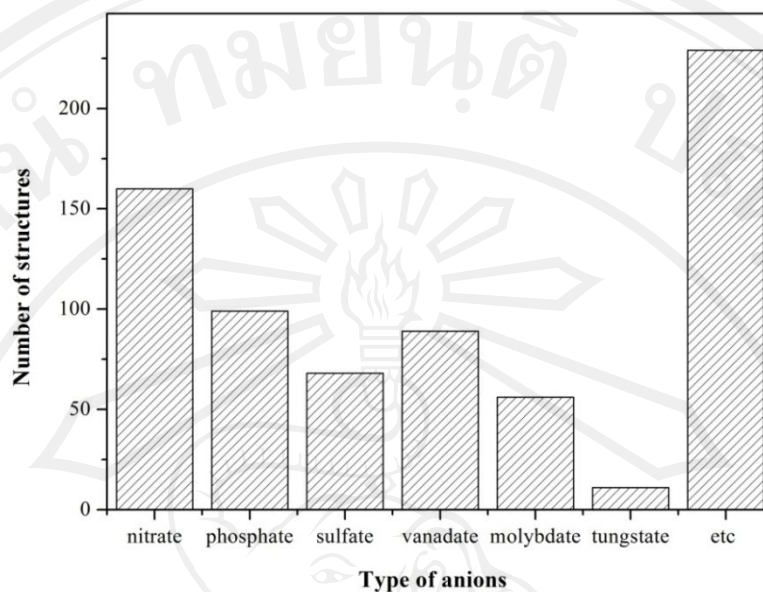


Figure 1.5 Numbers of Co-polyamine hybrid frameworks deposited in Cambridge Structure Database, during 1957 – May, 2012 [24].

Besides vanadates, sulfate is also intriguing in functioning as the bridging anions. New cobalt sulfates frameworks where the sulfate acts really as quadridentate bridging ligand is scarce, although it does share common tetrahedral coordination geometry with the pronounced zeolitic building units; $[\text{SiO}_4]$ and $[\text{AlO}_4]$. The relatively high electron density on the sulfate anion with most of the electron clouds localized around the sulfur central atom hinders the formation of coordinate covalent bond between the sulfate anion and the transition metal *via* oxygen bridges [37]. Many transition metal sulfates have 1-D or 2-D structures, and it has been observed that the formation of 3-D extended sulfate networks is difficult [44–46].

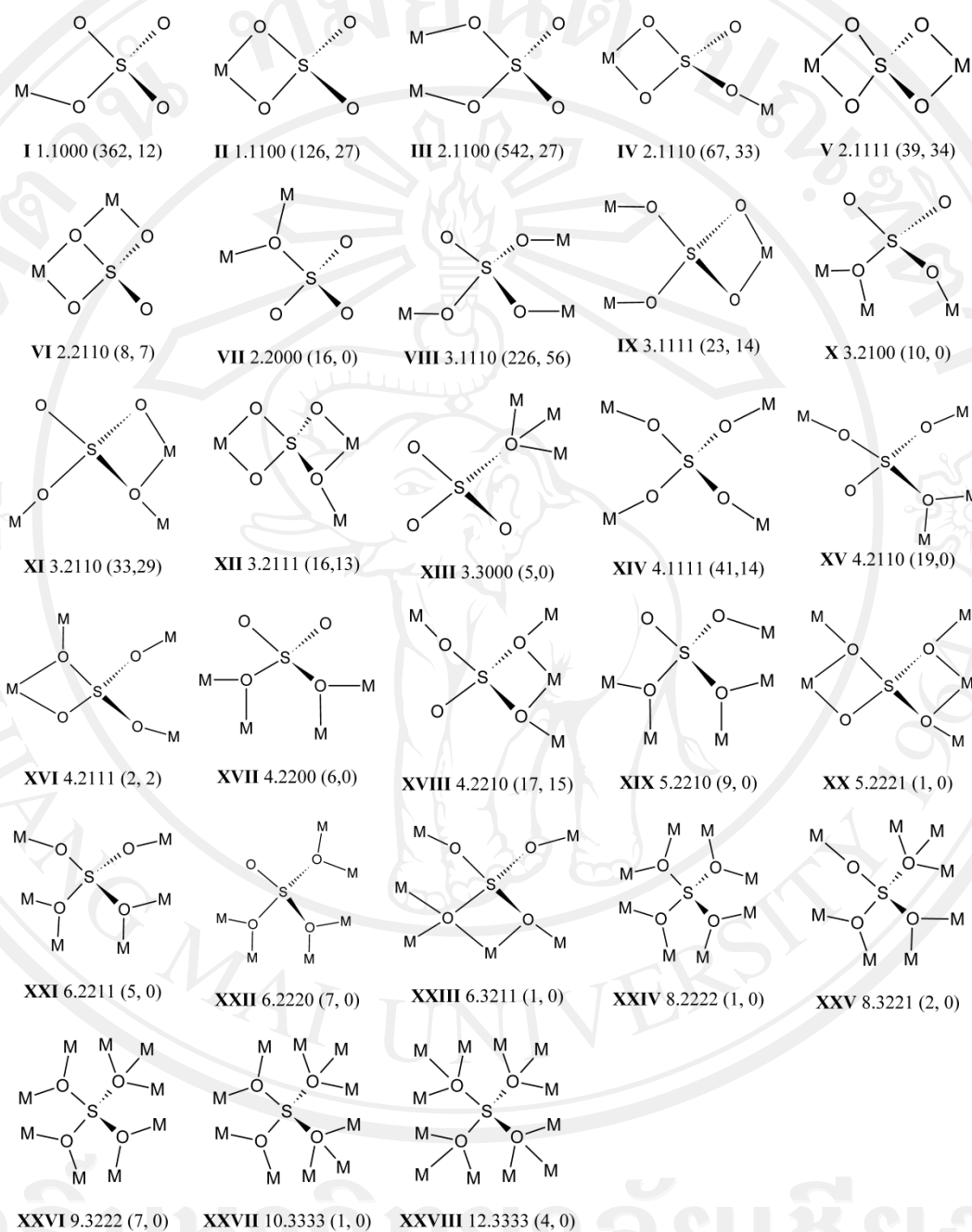


Figure 1.6 Diagrams showing different coordination modes reported to the Cambridge Structure Database for the sulfate anions with corresponding Harris notations. Figures in parentheses are numbers of the deposited structures for any metals (former) and lanthanides (latter).

In reference to the Cambridge Structure Database, numbers of the reported coordination modes of the sulfate nonetheless increased drastically: eight modes in 2003 [47] to eighteen modes in 2009 [48], and twenty-eight modes in 2012 [24]. Figure 1.6 depicts various modes of coordination with the numbers of the corresponding metal–organic framework structures in brackets. Within reported cobalt sulfate – polyamine hybrid frameworks, the sulfate anions may function as the counter anions to neutralize the framework charge [49], the monodentate ligand to decorate the framework as a pendant [44] and the multimode bridging ligand (bidentate, tridentate and quadridentate) to link adjacent metal centers and extend the framework structure [50, 46].

1.4 Recent overview on the lanthanide metal–organic hybrid materials

Besides the first row transition metals, the second and third row transition elements have very recently presented themselves in this competitive research field. Lanthanide series (Ln), for example, comprise fifteen elements from lanthanum (La) to lutetium (Lu), with atomic numbers ranging from 57 through 71. The elements in this series have attracted the study because of the high coordination number and the inherent flexibility of their coordination geometries, resulting in the unusual hybrid frameworks and unique optical properties arising from their *f-f* electronic transitions [51]. Moreover, their potential applications as magnetic materials, molecular sensors and luminescent materials [52, 53] are regarded. Since 1960 until present, there are more than 4,500 structures deposited in the Cambridge Structure Database as shown in Figure 1.7 [24]. It can be obviously seen that the number of lanthanide metals hybrid with O-donor ligands is higher than N-donor ligands. These results are in

accordance with hard–soft acid–base theory. Moreover it may well be noted that the elements occur solely as trivalent cations (Ln^{III}), although various coordination geometries of seven to twelve-coordinative environment can be found. More details on the lanthanides–organic frameworks will be shown in Chapter 4, 5 and 6.

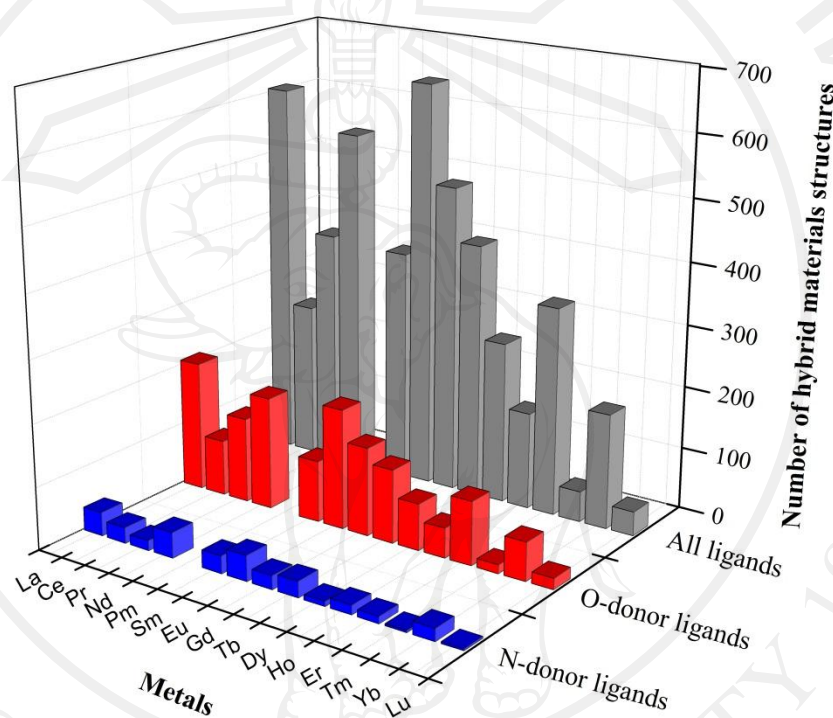
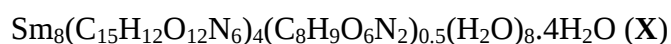
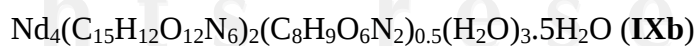
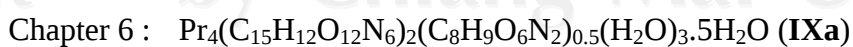
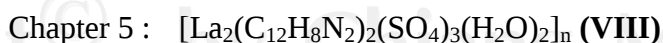
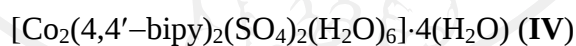
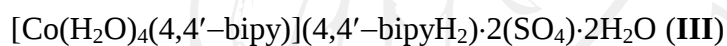
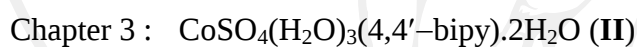
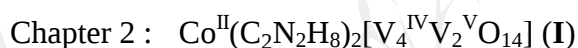


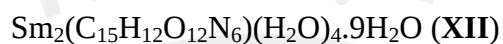
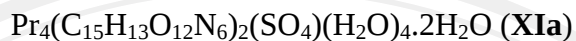
Figure 1.7 Numbers of the lanthanide metals–organic hybrid frameworks deposited in Cambridge Structure Database, during 1957 – May, 2012 [24].

Despite of a discovery of hybrid framework structures, the understanding of the functions of both inorganic and organic component in establishing the framework registry as well as the interaction patterns between the N–donor or O–donor ligands and the transition metals in various coordination environments are yet far from complete. Furthermore, the self-assembly of the structural building components occurring through several types of synergistic interactions between the inorganic and

organic moieties such as coordinate covalent bonds, hydrogen bonds, van der Waals interactions, hydrophilic-hydrophobic interactions and π - π interactions has to be rationalized. The studying of these interactions will provide the understanding of self-assembling process of the constructive compartments. Consequently, this information will certainly be significant in the design of functional materials with even complex structures and unique properties.

In this research, we have succeeded in the synthesis and structural characterization of twelve new structures of the Co-organic and Ln-organic hybrid structures using various -N and -O donor ligands. The twelve structures are grouped into five Chapters as listed:





1.5 Research objectives

1.5.1 To synthesize and grow single crystals of new first row transition metals and/or lanthanide metals hybridized with –N and/or –O donor ligands in molecular level.

1.5.2 To characterize the crystal structures and the interactions of the basic compartments.

1.5.3 To establish the understanding/knowledge on roles and interfacial interactions of the inorganic and organic components in the fabricated frameworks.

1.5.4 To study physical and chemical properties, *e.g.* thermal stability and luminescence properties, of the new compounds, and to rationalize the corresponding structure – properties relation.

1.6 Research plan

[illegible]

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