SYNTHESIS, CRYSTAL STRUCTURES AND PHOTOLUMINESCENCE STUDIES OF METAL COMPLEXES CONTAINING LIGANDS DERIVED FROM DIELS-ALDER ADDUCT

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by

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TABLE OF CONTENTS

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATION AND SYMBOLS

^{o}	degrees
Å	Angstrom, 1×10^{-10} m
Anal.	analysis
^{o}C	degrees celcius
δ	chemical shift in ppm
σ	sigma
π	pi
λ_{ex}	excitation
λ_{em}	emission
α	crystallographic unit-cell angle between axes b and c
β	crystallographic unit-cell angle between axes a and c
γ	crystallographic unit-cell angle between axes a and b
^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon-13 nuclear magnetic resonance
Calc.	calculated
d	doublet
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DMSO-d_6	deuterated dimethylsulfoxide
L	ligand
m	multiplet
t	triplet
s	singlet

SINTESIS, STRUKTUR HABLUR DAN KAJIAN KEFOTOPENDARCAHAYAAN KOMPLEKS LOGAM YANG MENGANDUNGI LIGAN TERBITAN OLEH ADUK DIELS-ALDER

ABSTRAK

Tindak balas kondensasi antara aduk Diels-Alder melalui antrasena dan maleik anhidrida dengan β-alanina dan asid 3-aminobenzoik, masing-masing membawa kepada pembentukan sebatian baru yang dinamakan *N*-3-(9,10-dihidroentanoantrasena-11,12-dikarbozimida)asid propanoik (**HL_1**) dan *N*-3-(9,10-dihidroentanoantrasena-11,12-dikarbozimida)asid benzoik (**HL_2**). Tindak balas satu bekas antara **HL_1** dengan kuprum(II) asetat berupaya membentuk kompleks mononuklear, $[Cu\mathbf{L_1}(H_2O)_3]$ (**1**). Dengan meninggalkan hablur biru **1** dalam wap metanol berkepekatan tinggi telah menghasilkan hablur hijau pudar kompleks dinuklear, $[Cu_2(\mu\text{-}\mathbf{L_1})_4(MeOH)(H_2O)]$ (**2**). Pemerhatian ini menunjukkan bahawa wap-pelarut telah membantu transformasi hablur-tunggal-ke-hablur-tunggal (SCSC) yang mendorong pertukaran nukleariti dari kompleks Cu(II) mononuklear ke dinuklear. Fenomena ini disebabkan oleh penyingkiran/pertukaran molekul air/pelarut dan penyusunan semula struktur berikutnya dalam fasa berhablur. Dengan menjalankan tindak balas sintesis hidrotermal di antara **HL_2** dan kuprum(II) asetat, pembentukan kompleks dinuklear $[Cu_2(\mu\text{-}\mathbf{L_2})_4(H_2O)_2]$ (**3**) telah diperolehi di mana penyusunan strukturnya adalah seakan sama dengan **2**, dengan koordinasi adalah molekul air dalam **3** dan bukannya metanol. Tindak balas di antara **HL_1** dan nikel(II) asetat pula menghasilkan pembentukan koordinasi polimer 1-D, $[Ni(\mathbf{L_1})_2(\mu\text{-}H_2O)_2(H_2O)_2]_n\cdot nH_2O$ (**4**). Sementara itu, kedua-dua tindak balas antara argentum(I) asetat dengan **HL_1** dan **HL_2** masing-masing menghasilkan

pembentukan $[Ag_2(\mu\text{-}\mathbf{L_1})_2(H_2O)_2]$ (**5**) dan $[Ag_2(\mu\text{-}\mathbf{L_2})_2(H_2O)_2]$ (**6**). Tidak disangka, tindak balas antara argentum(I) asetat, **HL₂** dan 4,4'-bipiridina telah membentuk kompleks $[Ag(\mu\text{-}\mathbf{L_2})(4,4\text{-bpy})]_n$ (**7**) sebagai strukur polimer 1-D dengan ion pusat argentum(I) menunjukkan geometri satah segi empat sama yang sebelumnya jarang berlaku, iaitu berbeza daripada geometri umum tetrahedron dalam sistem d^{10}. Selain itu, tindak balas terbium(III) nitrat pentahidrat dengan $\mathbf{HL_1}$ dan $\mathbf{HL_2}$, masing-masing menghasilkan pembentukan kluster dinuklear, $[Tb_2(\mu\text{-}\mathbf{L_1})_2(\mathbf{L_1})_4(H_2O)_4(MeOH)_2]$ (**8**) dan $[Tb_2(\mu\text{-}\mathbf{L_2})_2(\mathbf{L_2})_4(H_2O)_2(MeOH)_2]$ (**9**). Menariknya dalam kajian kefotopendarcahayaan, kompleks **5** mendedahkan bahawa dinuklear ini mempunyai potensi sebagai pengesan suhu ratiometrik pendarkilau yang mempunyai sifat dua pancaran cerapan dengan pancaran maximum pada 415 dan 550 nm. Berbeza daripada **5**, kedua-dua kompleks **6** dan **7** hanya wujud cirian mono pancaran pada ~420 nm disebabkan oleh ketiadaan interaksi intermetalik argentofilik di dalam kompleks ini. Di samping itu, kedua-dua kompleks **8** dan **9** juga menunjukkan sifat kefotopendarcahayaan yang menarik dengan puncak pancaran intensiti pendarfluor tinggi pada 545 nm yang menghasilkan pancaran hijau.

SYNTHESIS, CRYSTAL STRUCTURES AND PHOTOLUMINESCENCE STUDIES OF METAL COMPLEXES CONTAINING LIGANDS DERIVED FROM DIELS-ALDER ADDUCT

ABSTRACT

A condensation reaction between the Diels-Alder adducts of anthracene and maleic anhydride with β-alanine and 3-aminobenzoic acid, facilitates the formation of new compounds, namely *N*-3-(9,10-dihydroanthracene-11,12-dicarboximide)propanoic acid (**HL$_1$**) and *N*-3-(9,10-dihydroanthracene-11,12-dicarboximide)benzoic acid (**HL$_2$**), respectively. A one pot-reaction of **HL$_1$** with copper(II) acetate afforded the formation of mononuclear complex, $[\mathrm{Cu}\mathbf{L_1}(\mathrm{H_2O})_3]$ (**1**). By leaving the blue crystal of **1** in high concentrated methanolic vapor resulting the formation of pale green crystal of dinuclear complex, $[\mathrm{Cu_2}(\mu\text{-}\mathbf{L_1})_4(\mathrm{MeOH})(\mathrm{H_2O})]$ (**2**). This observation indicated the solvent-vapor mediated single-crystal-to-single-crystal (SCSC) transformation that promoted nuclearity cross-over from mononuclear to dinuclear of Cu(II) complex. This phenomenon due to the removal/exchange of water/solvent molecules and subsequent structural rearrangement in the crystalline phase. By undertaking hydrothermal synthesis reaction of **HL$_2$** and copper(II) acetate, dinuclear complex $[\mathrm{Cu_2}(\mu\text{-}\mathbf{L_2})_4(\mathrm{H_2O})_2]$ (**3**) was obtained, in which the structural arrangement is almost similar to **2,** with coordinated of water in **3** instead of methanol. The reaction of **HL$_1$** and nickel(II) acetate resulted the formation of 1-D coordination polymer, $[\mathrm{Ni}(\mathbf{L_1})_2(\mu\text{-}\mathrm{H_2O})_2(\mathrm{H_2O})_2]_n\cdot n\mathrm{H_2O}$ (**4**). Meanwhile, both reaction between silver(I) acetate with **HL$_1$** and **HL$_2$** allowed the formation of dinuclear complexes $[\mathrm{Ag_2}(\mu\text{-}\mathbf{L_1})_2(\mathrm{H_2O})_2]$ (**5**) and $[\mathrm{Ag_2}(\mu\text{-}\mathbf{L_2})_2(\mathrm{H_2O})_2]$ (**6**), respectively. Unexpectedly, the reaction between

silver(I) acetate, $\mathbf{HL_2}$ and 4,4'-bipyridine formed a complex $[\mathrm{Ag}(\mu\text{-}\mathbf{L_2})(4,4\text{-bpy})]_n$ (**7**) as 1-D polymeric structure with the central silver(I) ions display unprecedented square-planar geometry, which is outlier from common tetrahedral geometry of d^{10} system. Besides, the reaction of terbium(III) nitrate pentahydrate with $\mathbf{HL_1}$ and $\mathbf{HL_2}$, lead the formation of dinuclear cluster for both lanthanide complexes, $[\mathrm{Tb_2}(\mu\text{-}\mathbf{L_1})_2(\mathbf{L_1})_4(\mathrm{H_2O})_4(\mathrm{MeOH})_2]$ (**8**) and $[\mathrm{Tb_2}(\mu\text{-}\mathbf{L_2})_2(\mathbf{L_2})_4(\mathrm{H_2O})_2(\mathrm{MeOH})_2]$ (**9**), respectively. Remarkably, in the photoluminescence studies, complex **5** reveals that this dinuclear has potential as a ratiometric luminescent temperature sensor that features dual emission property with emission maxima at 415 and 550 nm. In contrast to **5**, both complexes **6** and **7** only appeared a mono emission characteristic at ~420 nm due to the absence of intermetallic argentophilic interactions in these complexes. On the other side, both complexes **8** and **9** also display fascinating photoluminescence property with the highest fluorescence intensity emission peak at 545 nm that resulted in green emission.

CHAPTER 1

INTRODUCTION

1.1 Coordination chemistry

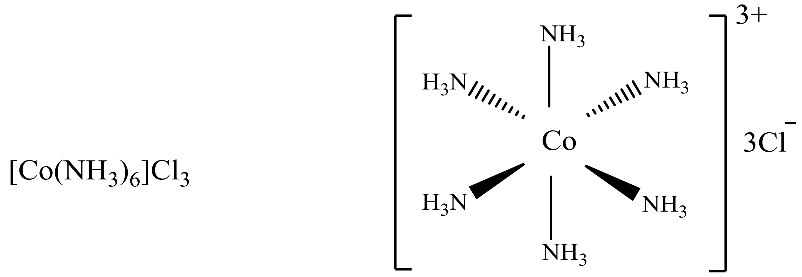
Coordination chemistry is a part of chemistry that comprises the studies of structural, chemical, magnetic and spectral properties of coordination compounds [1]. Coordination compound or better known as coordination complex or metal complex is a structure that consists of central atom, bonded to organic moiety called ligands [2]. The basic concept of covalent bond was introduced by G. N. Lewis that provides the explanation regarding electron pair donor (**:**D) and electron pair acceptor (A), which employed in the formation of coordination bond (Scheme 1.1) [3]. Hence, the essential features of coordination compounds are the metal ion that acting as a Lewis acid (electron pairs acceptor), and a ligand (electron pairs donor) that functioning as a Lewis base [4]. Furthermore, to achieve the formation of coordination metal complexes, the metal ion must contain an empty orbital in order to accept an electron pair from the ligand. The numbers of coordination bonds formed are largely depending on the availability of the empty orbitals within the metal ion [5].

$$A + : D \rightarrow A : D$$

Scheme 1.1: General representation of covalent bond.

Back to the half nineteenth century, discoveries of coordination compounds were few, distracted and produced with uncertain evidences [6]. At the same time, coordination compounds were also found important through their applications in biological systems such mechanism of chlorophyll and heme [7]. Nearly three centuries ago, a bright blue pigment, known as Prussian Blue was prepared accidentally by Diesbach. This compound was the first man-made coordination compound that was used as a dye due to its intense color. With the formula of $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$, the derivatives of Prussian Blue have been extensively developed since then [8]. Moreover, another interesting finding of coordination compound was recorded in 1957 by German chemist, Andreas Libavius that observed the formation of blue solution of tetraamminecopper(II) ion, $[Cu(NH_3)_4]^{2+}$. The latter was observed when sal ammoniac (NH_4Cl) in lime water was left to react with brass [9].

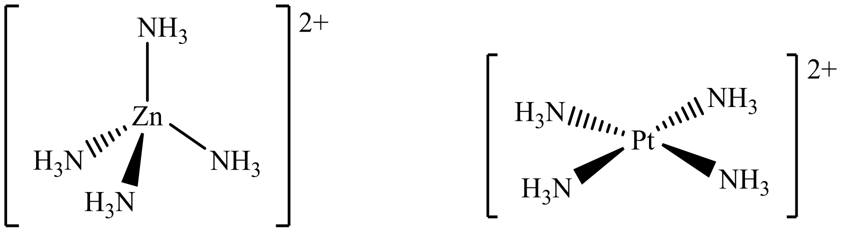
In 1893, Alfred Werner brought forward the coordination chemistry theory by explaining the coordination number as the number of atoms surrounding the central atoms. Werner also postulated the ligands can be replaced by any other suitable groups or ligands [10,11]. Werner suggested that there are two types of valences, which are primary valence (ionizable) and secondary valence (nonionizable) which are available for spatial directed in space around a central metal atom, combined to form a complex [12,13]. By applying this theory, Werner reported the constitutional for compound $[Co(NH_3)_6]Cl_3$ that had been studied by other researchers before (Figure 1.1). The complex $[Co(NH_3)_6]Cl_3$ comprised as a discrete unit (complex cation), which coordinated to six ammonia molecules, resulting a 3+ central atom. The charge is then balanced with the presence of three chloride anions in the lattice, which thus convincing for six coordination number as an octahedral in structure [13]. For instance, coordination number four belongs to tetrahedral and square planar geometry (Figure 1.2) [14].



$[Co(NH_3)_6]Cl_3$

(i) Constitutional (ii) Configuration

Figure 1.1: Werner complex of $[Co(NH_3)_6]Cl_3$.



Tetrahedral Square Planar

Figure 1.2: Configurations of coordination number four.

1.2 Ligands in coordination complexes

Researches on coordination chemistry are studies about all alkali and alkaline-earth metals, transition metals, lanthanides, actinides and metalloids [15]. Moreover, transition metal and lanthanide complexes have attracted wide interest owing to their potential applications in numerous areas, such as in medicinal, catalytic and optical studies [16-18]. Furthermore, the flexibility of transition and lanthanide metals may lead to different molecular architectures in the presence of either chelating or bridging ligand which resulting in interesting structures and potentially useful chemical and physical properties. The design of the reactions and also selectivity of the ligands are crucial in order to obtain desired complexes with aforementioned potential applications [19].

Ligands play the main role in determining the structure of metal complexes. Among of those reported ligands, carboxylic acid ligands have been found to be widely used in the formation of coordination complexes including mononuclear, cluster complexes or coordination polymers due to their tendency to exhibit more conformational and coordination versatility [20-23]. Derivatives of carboxylic acid such as esters, amides, anhydrides and acid halides are relatively dominant in natural system and synthetic organic chemistry [24].

Upon deprotonation and coordinated with metal ions, the nomenclature of such ligand will be known as carboxylate. The versatility of carboxylate can be observed by the ability of this group to adopt various denticity modes, ranging from monodentate to tetradentate (Figure 1.3). Theoretically, the highest denticity for a discrete carboxylate group is four (μ_4-bridging mode), in which the four metal ions are bridged by only one carboxylate moiety (Figure 1.3(vi)) [25]. For the monodentate or unidentate coordination mode, in most cases, the intermolecular hydrogen bond is formed with the retaining nonionized carboxylate [26]. These thus opened to a variety of structures initiated by numerous types of coordination bonds and supramolecular interactions [27].

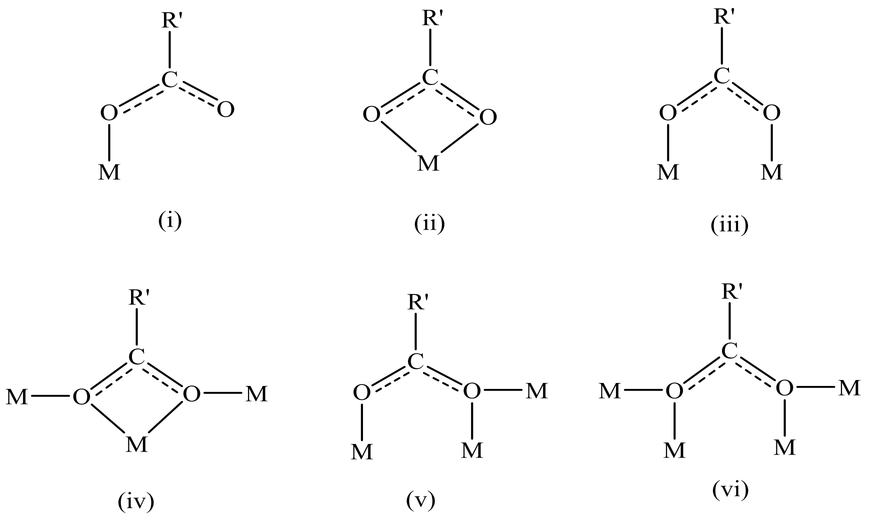


Figure 1.3: Versatility coordination modes of carboxylate ligands (R'COO^-; R'= Me, Ph) [25].

Undoubtedly, the presence of carboxylic ligand is important in designing coordination complexes including polynuclear clusters or coordination polymers especially with the presence of more than one carboxylic moiety in the ligand. With the presence of at least two carboxylic groups, the ligand may coordinate to two different metal ions, thus giving rise to high nuclearity polynuclear complexes or high dimensionality coordination polymers [28,29]. Such example being the uses of octadentenate carboxylic linker, 5,5′,5″,5‴-silanetetrayltetraisophthalic acid (H_8L) as a precursor for the formation of microporous 3D coordination polymers complexes with several metal ions, prepared *via* hydrothermal synthesis (Figure 1.4) [30]. In the formation of respective coordination polymers, the H_8L ligand were documented to either fully deprotonated or partially deprotonated in the form of L^{8-} or H_2L^{6-}, respectively.

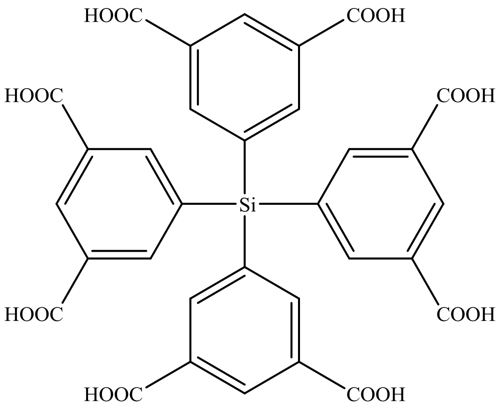


Figure 1.4: Structure of H_8L *as a precursor for the formation of various 3D coordination polymers.*

However, there are also examples of mononuclear complexes formed despite more than one carboxylic group are presence within the ligand. Rahazat *et al.* reported the formation of mononuclear complex, $[Ag(PPh_3)_2(2,3\text{-}pyCOO]$ that was prepared from the reaction between $[Ag(PPh_3)_2OAc]$ with 2,3-pyridinedicarboxylic acid. Despite that two carboxylic groups are presence in the structure of 2,3-pyridinedicarboxylic acid, only one of them was deprotonated and bonded to metal ion, giving rise to the formation of discrete mononuclear complex (Figure 1.5) [23]. As expected in this structure, for the protonated carboxylic group (O4-H4), the formation of intramolecular hydrogen bond was observed with the adjacent oxygen atom (O2). This thus indicates that, even coordination bond is not formed with metal ion, the presence of carboxylic group may as well facilitate the formation of supramolecular interaction, especially hydrogen bonding network.

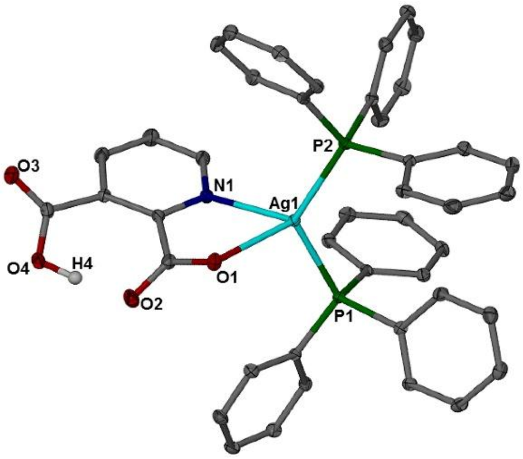


Figure 1.5: Structure of [Ag(PPh_3)$_2$(2,3-pyCOO)] with ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity [23].

On the other side, Jassal *et al.* documented the multifunction ligand of dinitrobenzoic acid that have potential in variety binding modes in favor to construct coordination polymer (Figure 1.6) [31]. Remarkably in this project, a 1-D polymeric structure of copper(II) complex, $[Cu(\mu_2\text{-}\mathbf{L})_2.(H_2O)_2]_n$ (where **L** = 3,5-dinitrobenzoates) was achieved by single-crystal-to-single-crystal, succeeding from dimeric structure of $[Cu(\mu_2\text{-}\mathbf{L})_2.H_2O]_2.(C_2H_3N_2)$ by losing acetonitrile molecule through their structural transformation. The copper(II) ion display as square planar geometry (Figure 1.7), surrounded with two water molecules and two benzoate ligand that acts as monodentate ligand. Noteworthy, the coordinated water molecules, O1W and O2W assemble intermolecular hydrogen bond interactions as well as both nitro group of ligands which then responsible to form 2D structure of complex (Figure 1.8).

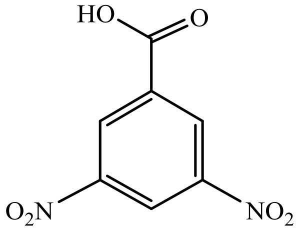


Figure 1.6: Structure of 3,5-dinitrobenzoic acid used as a ligand (HDNB) in metal-organic frameworks.

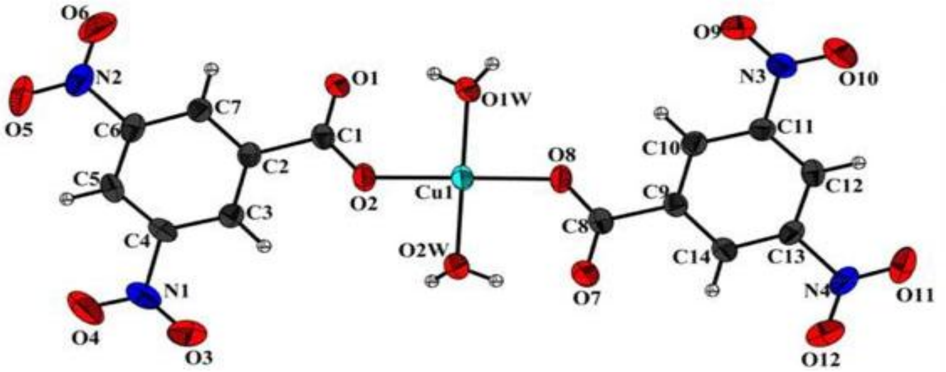


Figure 1.7: Structure of $[Cu(\mu_2\text{-}L)_2.(H_2O)_2]_n$ with ellipsoids shown at 50% probability [31].

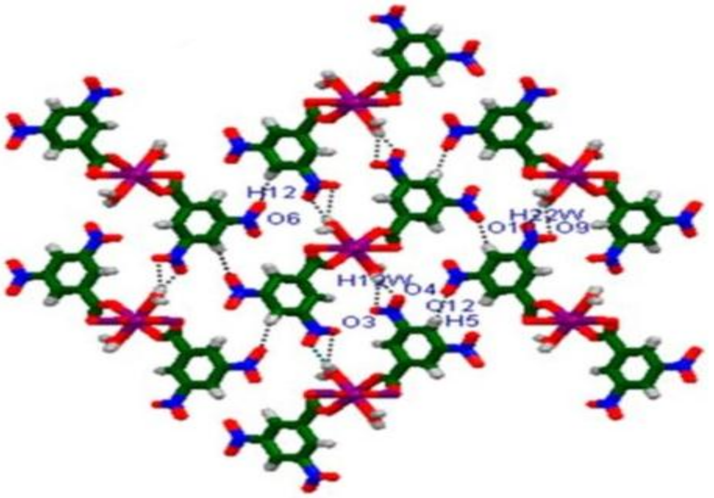
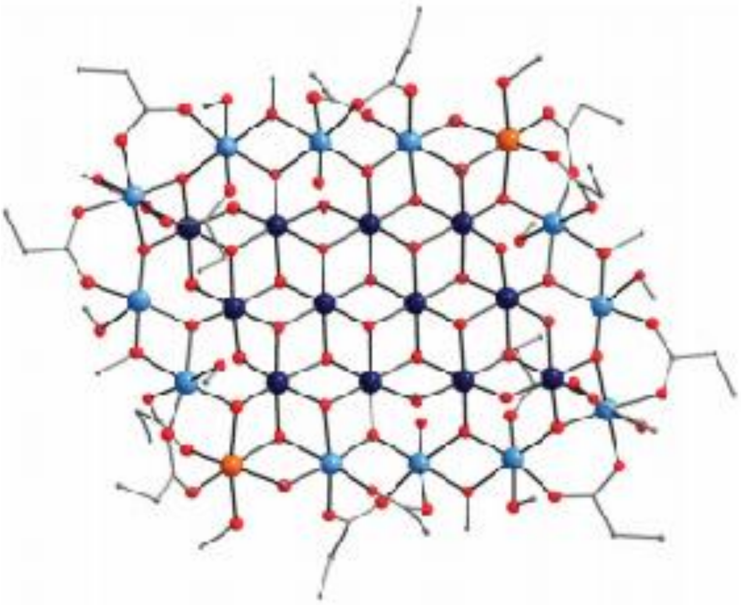


Figure 1.8: A 2D network of $[Cu(\mu_2\text{-}L)_2.(H_2O)_2]_n$ with intermolecular hydrogen bonds [31].

1.3 Classes of coordination complexes

Coordination complexes can be classified to three classes which are; (i) discrete mononuclear complexes; (ii) discrete polynuclear clusters; and (iii) coordination polymers [32]. The mononuclear complexes are belonging to the compounds that contain only one metal ion within the structure, despite the number of the ligand can be varied [33]. Polynuclear clusters are the metal complexes with at least two metal ions within the molecules, bridged by a ligand which usually known as well as discrete molecules [34,35]. Among the clusters are binuclear, trinuclear, tetranuclear, pentanuclear and so on; depending on the number of the metal ions within the structure (Figure 1.9). Those complexes with carboxylic groups are known to be the most abundance polynuclear clusters since this group can easily bonded to more than one metal ions per carboxylate moiety [36].

(a)



(b)

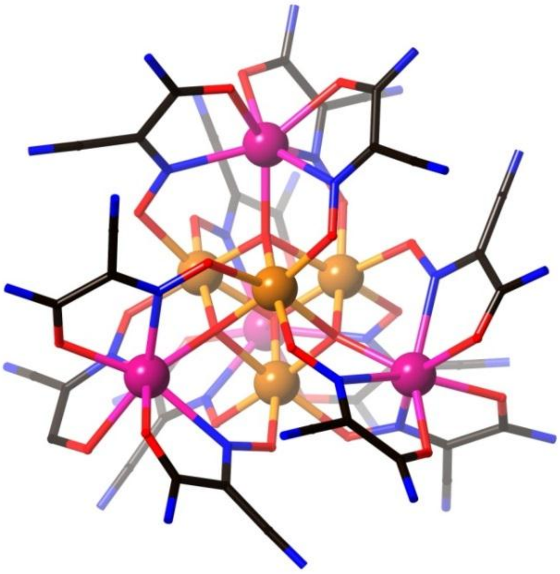


Figure 1.9: Core structures of (a) $Mn_{24}Ni_2$ *[37]; and (b) octanuclear mixed-valent* $Mn^{II}_4Mn^{III}_4$ *cluster [38].*

Moreover, coordination polymers were noticeable in early 1960s, invented by Karl Ziegler and Giulio Natta. Among others, these compounds have a remarkable interest owing to their potential, due to their fascinating composition, architecture and reactivity [39-41]. Most coordination polymers 'self-assemble' whereby the reactants form the thermodynamically most stable products under the chosen conditions [42,43]. Such example when the ligand being a dominant factor in the preparation of coordination polymer is the formation of $[Cu(nca)_2(pyz)]_n$ (where nca = nitrocyanamide; pyz = pyrazine) (Figure 1.10) [44]. In this structure, both ligands are behaving as a μ_2-bridging ligand, giving rise to the formation of a 2D sheet. Noteworthy, for all coordination polymer structures, they may exist or can be described as a 1D chain, 2D sheets or 3D networks [43]. Rather than suitable bridging ligands, in most cases, the formation of coordination polymers are also depending on the methods used to prepare such complexes. Usually harsh conditions such as hydrothermal synthesis was used to achieve the formation of high dimensionality coordination polymers with certain properties [45].

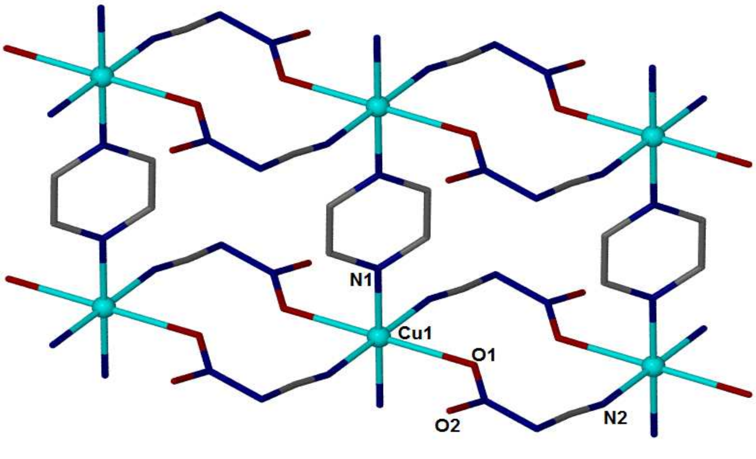


Figure 1.10: A 2D sheet structure of $[Cu(nca)_2(pyz)]_n$*. [44].*

1.4 The Diels-Alder Adduct

The Diels-Alder reaction has been a major interest and controversy during the half century since it was first discovered by Otto Diels and Kurt Alder in 1928 [46,47]. The Diels-Alder or [4+2] cycloaddition is the reaction that involving conjugated 4π-electron system called diene and 2π-electron system called dienophile (Figure 1.11) [48]. Diels-Alder is known as a ‘click’ group due to its versatility, efficient and selective synthesis [49]. Thus, this protocol becomes one of the most important reaction procedures in organic synthesis especially in developing cyclic structures withal a strategy to generate bicyclic compounds [50].

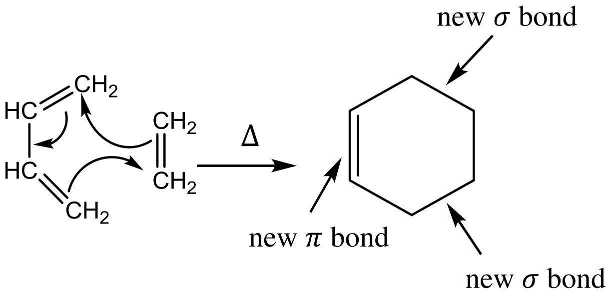


Figure 1.11: General representation of Diels-Alder reaction.

Generally, cycloaddition can be prepared under a variety experimental conditions in which both thermal and pressure were needed in some cases for unreactive diene and dienophile, assisted by Lewis acid, Bronsted acid, microwaves or catalyst [51-54]. In particular, cycloaddition is the reaction to form cyclic adduct by having two π reactants along with other π components to form new σ bonds. Herein, some of the cycloaddition products aside from [4+2], Diels-Alder reactions are shows in Figure 1.12 [55].

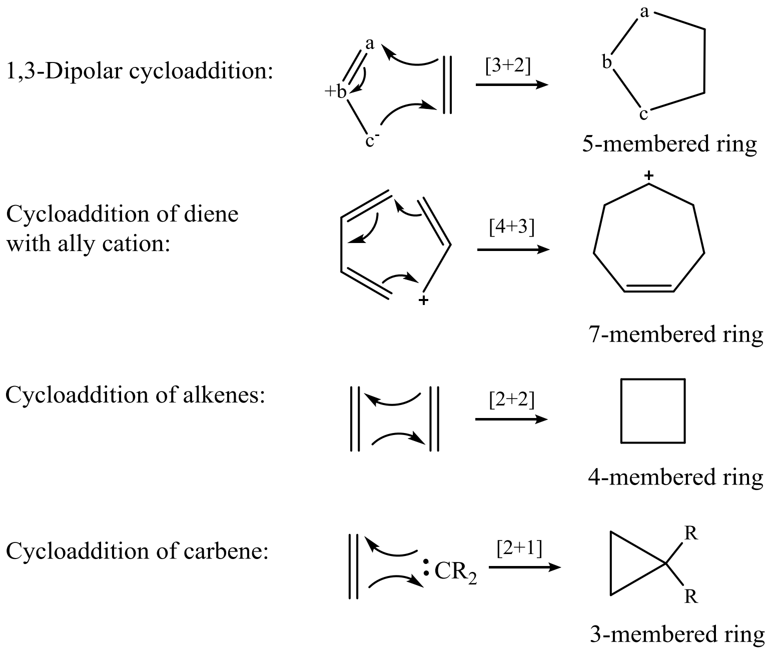


Figure 1.12: Examples of cycloadditions.

The usefulness of Diels-Alder reaction in organic synthesis benefited from their versatility. Moreover, by varying the nature of diene and dienophile, many types of ring structures can be created [56]. The cyclic movement of electron pairs in between electron-rich diene will react with the electron-poor alkene (dienophile) to yield unsaturated six-membered ring product [57]. Hence, Figure 1.13 illustrates an example for the significant reaction of Diels-Alder that leads to the formation of cyclohexene derivative as reported by Otto Diels and Kurt Alder [58]. Moreover, the Diels-Alder reaction can be achieved by concerted mechanisms including simultaneous bond forming and bond breaking. This thus implies a very clean and high yield chemistry which is important to realistic repetitive cycle thermochemical applications [59].

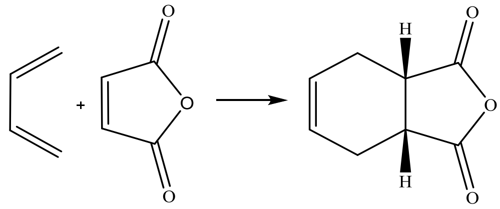


Figure 1.13: Diels-Alder reaction in between 1,3-butadiene with maleic anhydride reported by Otto Diels and Kurt Alder [58].

By understanding the frontier molecular orbital theory (FMO), the reactivity, regioselectivity and stereochemistry of cycloaddition reaction are determined by the suprafacial in phase interaction of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) [60,61]. Therefore, the lower the energy difference between frontier orbitals, the greater interaction of orbitals is achieved, thus simultaneously increases the opportunity for reactions to occur [62]. This statement indicates that the higher the energy of HOMO (diene) will facilitate the electron to be removed and the lower LUMO (dienophile) will assist the electron to be easily transferred, respectively (Figure 1.14).

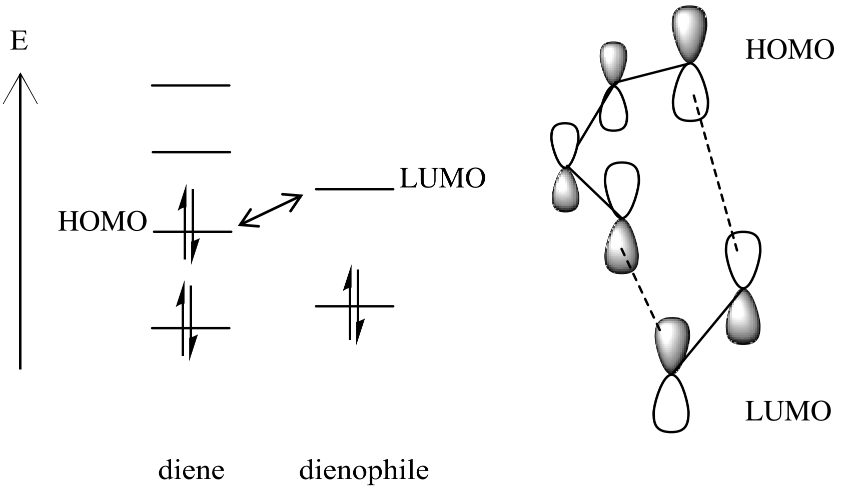
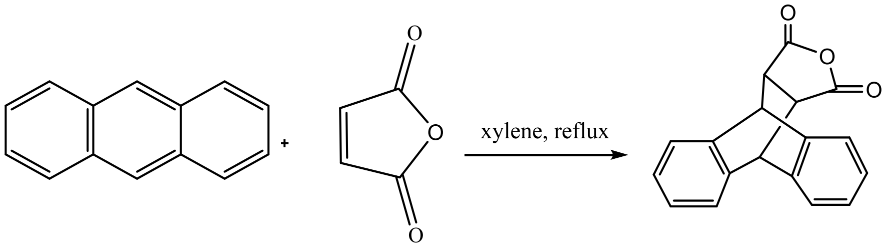
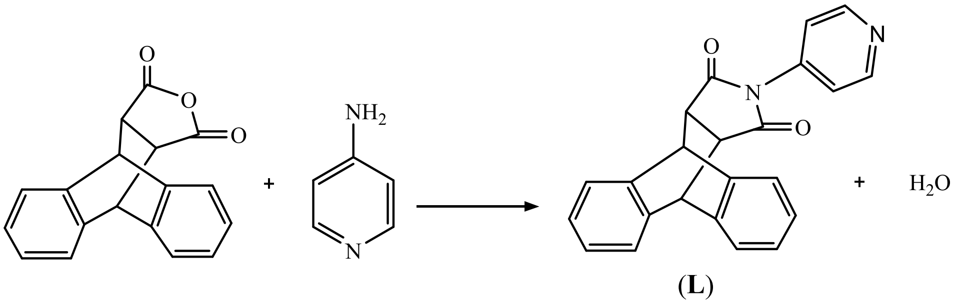


Figure 1.14: HOMO-LUMO energy separation of 1,3-butadiene and ethene [48].

The remarkable of Diels-alder reaction is applied in order to generate the novel aromatic cycloadducts that usually have an interesting emissive property [63]. Herein, Chan *et al.* reported the synthesized of *N*-(4-pyridinyl)-9,10-dihydroethanoanthracene-11,12-dicarboximide, **L** by involving the aforementioned Diels-Alder adduct of anthracene and maleic anhydride, as a ligand precursor (Scheme 1.2). The targeted compound was the result of condensation reaction between 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride and 4-aminopyridine (Scheme 1.3). Furthermore, the formed **L** compound was then used to prepare a dinuclear copper(I) complex, [Cu_2I_2**L**$_2$(MeCN)$_2$] as shown in Figure 1.15 [64]. As hypothesized before, the presence of electron rich component in ligand **L** and with the addition of d^{10} ion, in this case, copper(I) ion, the cluster displayed a fascinating photoluminescence property which have brightly emissive complex at room temperature, showing an intense blue at room temperature (Figure 1.16).



Scheme 1.2: Synthesis of 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride from anthracene and maleic anhydride.



*Scheme 1.3: The formation of N-(4-pyridinyl)-9,10-dihydroethanoanthracene-11,12-dicarboxide (**L**).*

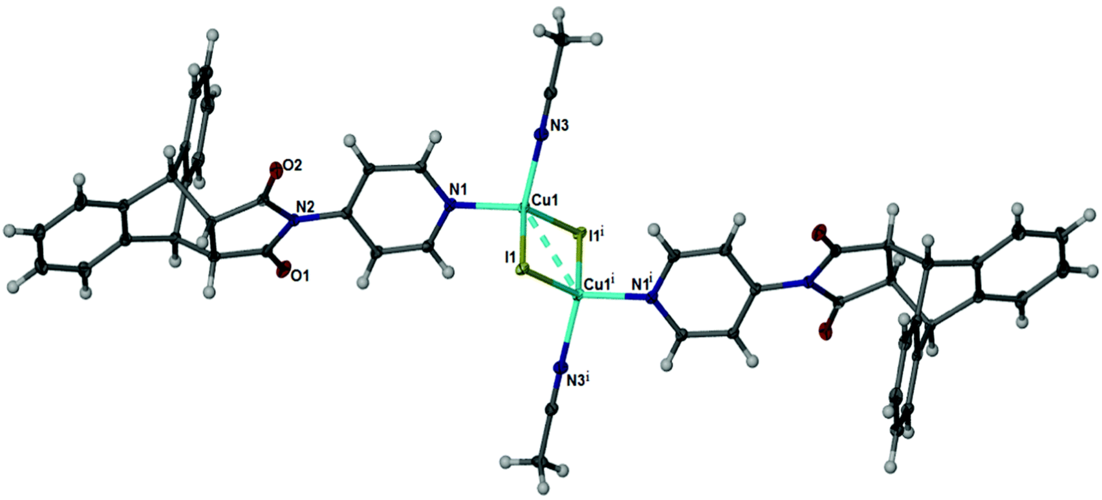


Figure 1.15: Structure of $[Cu_2I_2\mathbf{L}_2(MeCN)_2]$ with the ellipsoids shown at 50% probability [64].

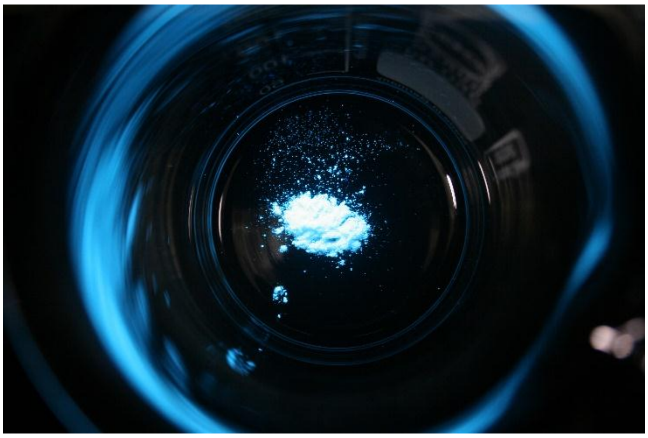
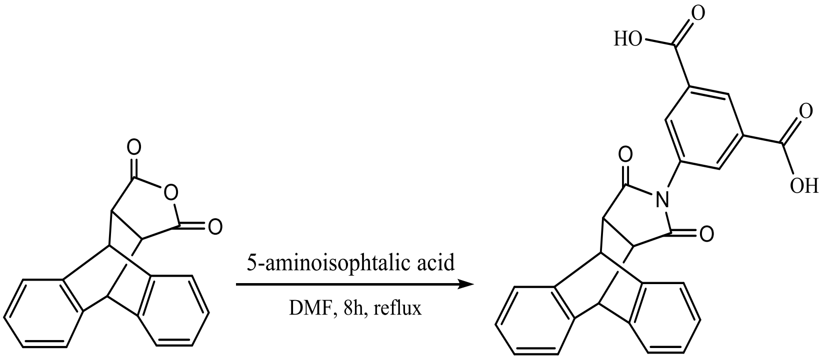
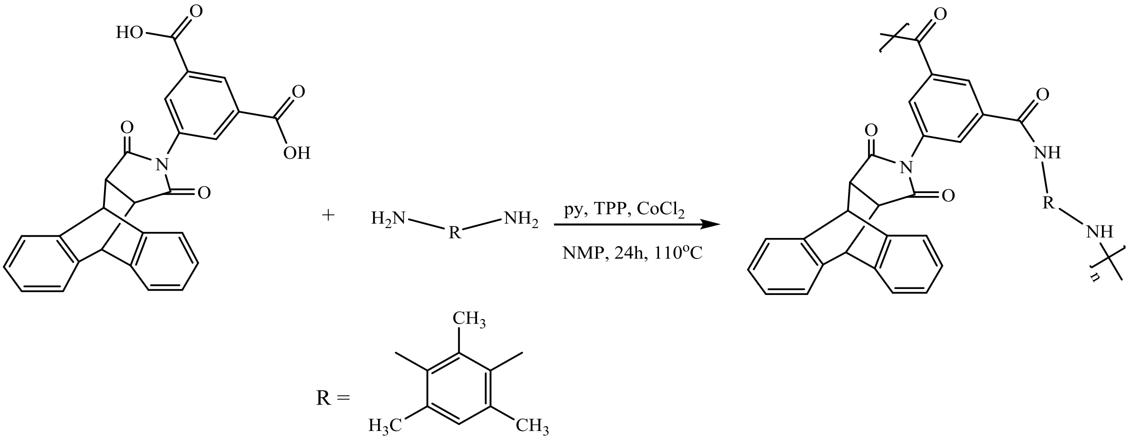


Figure 1.16: Photographs of the microcrystals of $[Cu_2I_2\mathbf{L}_2(MeCN)_2]$ *under the UV lamp* (λ_{ex} = *365 nm) at ambient room temperature [64].*

Moreover, the derivatives of Diels-Alder reaction was used as well to construct a wide range of polymeric materials [65]. In 2015, Santiago-Gracia *et al.* reported the synthesis of bulky dibenzobarrelene with 5-aminoisophthalic acid and 9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride in order to facilitate the formation of 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) isophthalic acid (Scheme 1.4). This molecule was then used as a pendant group to determine the novel polyamides (Scheme 1.5) [66,67]. Allied this, the versatility starting materials of maleic anhydride from Diels-Alder enhances the variety of functional materials that leads to more interesting desire molecules [68], worthwhile anthracene derivatives used compounds were found to be prior in designing the luminescence properties [69].



Scheme 1.4: Synthesis of 5-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamido) isophthalic acid from Diels-Alder framework.



Scheme 1.5: The synthesis routes of novel polyamides.

Nevertheless, even there are numerous products of Diels-Alder have been prepared before, only few were used as a precursor for the ligands in metal complexes. This is despite to the potential of this molecule to exhibit fascinating photoluminescence properties due to the higher number of delocalize electrons within the aromatic rings.

1.5 Preparation of metal complexes

Basically, the formation of coordination compounds can be achieved via several means, which the easiest method being a one-pot synthesis. Herein, both metal salt and ligand precursor are added together in a solvent and left to react at ambient room temperature. The products usually powder or crystalline materials will be deposited in the reaction mixture after certain period of time. In order to obtain the product in shorter period of time, the reactants can also be heated under reflux. Furthermore, advancements in latest technology and crystal engineering have manoeuvred numerous new techniques including hydrothermal/solvothermal synthesis, structural transformations, microwave assist synthesis and others.

In the middle of nineteenth century, the term of hydrothermal was first taken by British geologist, Sir Roderick Murchison in relating the action of water at high temperature and pressure of the earth's crust, thus leading the formation of various minerals and rocks [70]. Hydrothermal synthesis was designed for synthesizing inorganic materials in aqueous medium that allow the reaction to be conducted at elevated temperature with high pressure in a closed chamber [71,72]. The advantage of this technique is conducted for reactions that were unsuccessful at ambient room condition in order to force the reaction between the metal ion and ligand to allow the crystalline phases to be created. In addition, water is major important solvent as a medium to increase the solubility of desired compounds [70]. However, not all the compounds will show their solubility for water even at supercritical temperature thus this require others suitable solvent in the process [73].

Herein, usually the polynuclear metal cluster and high dimensionality coordination complexes will be formed through hydrothermal synthesis. For this method, the example being the work conducted by Mustafa *et al.* in which the formation of 1-D coordination polymer of complex $[\mathrm{Ag_2(PPh_3)(2tpCOO)_2}]_n$ (where $\mathrm{PPh_3}$ = triphenylphosphine; 2tpCOOH = 2-thiophenecarboxylic acid) was achieved by leaving the initially formed tetranuclear silver(I) complex within the mother liquor in a closed glass tube at 120 °C for two days (Scheme 1.6) [21]. In this structural transformation, the denticity of the carboxylate used is increased, from μ_3-bridging mode to μ_4-bridging mode (Figure 1.17).

$$\begin{tikzcd}
\mathrm{Ag(I)} + \mathrm{PPh_3} + \mathrm{2tpCOOH} \arrow[r] & {[\mathrm{Ag_4(PPh_3)_4(2tpCOO)_4}]} \arrow[d, "\text{Hydrothermal}"'] \\
& {[\mathrm{Ag_2(PPh_3)(2tpCOO)_2}]_n}
\end{tikzcd}$$

Scheme 1.6: Route formation of polymeric complex [21].

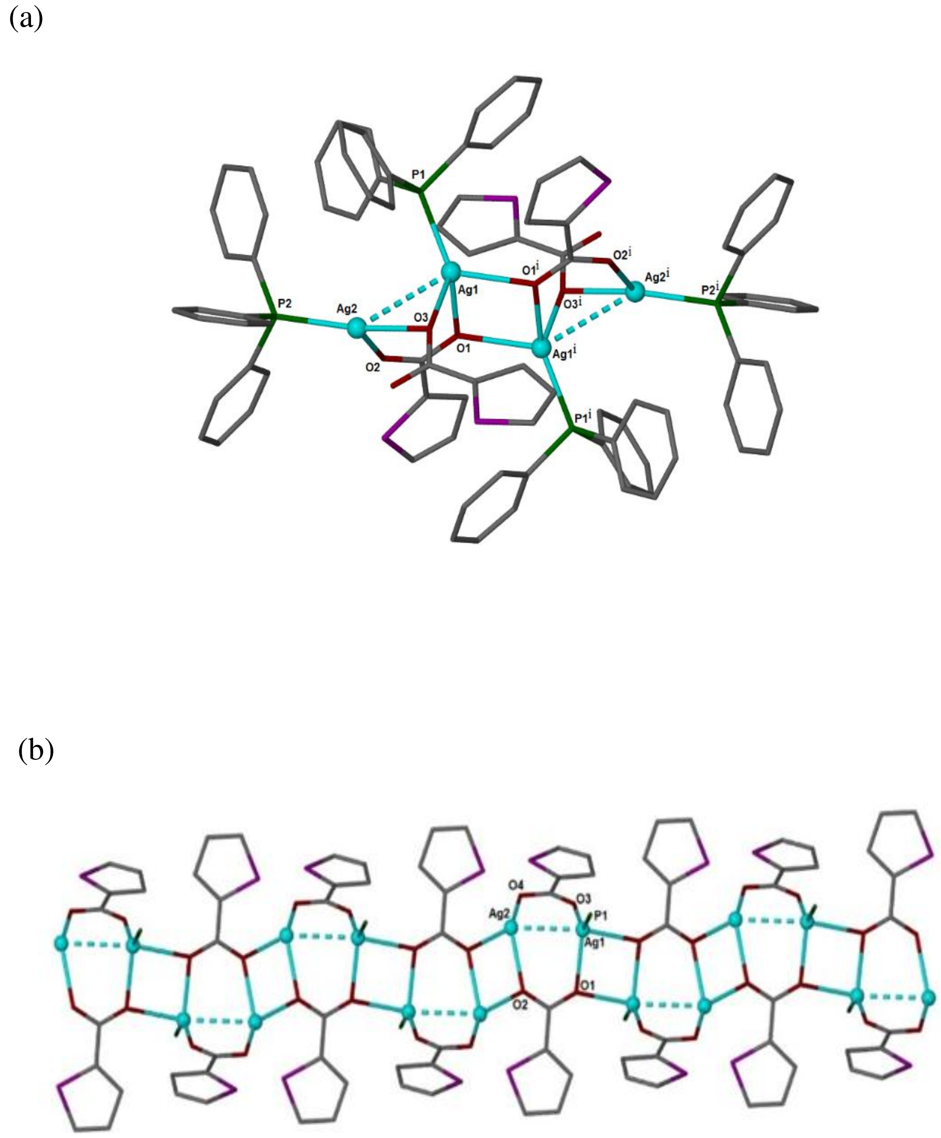


Figure 1.17: (a) Structure of tetranuclear [$Ag_4(PPh_3)_4(2tpc)_4$]. Upon leaving in a closed chamber at high temperature resulted the formation of; (b) A 1-D polymeric structure of [$Ag_2(PPh_32tpCOO)_2$]$_n$ [21].

Another method in preparing coordination compound is through structural transformation which is known as well as single-crystal-to-single-crystal (SCSC) transformation. The phenomena of SCSC transformation has been noticed long time ago, thereafter drawn great attention in extending their potential in many fields [74]. Generally, the SCSC transformation is described as solid-state phase transition in between different crystalline state whither the whole transformation process retained their crystal integrity and the long ranges structural order [75]. Through this process, single crystal is exposed to external stimuli such as solvent vapors, light, heat or pressure (Figure 1.18), thus, the changes of crystal color of SCSC were realized to have potential in sensor technology [76,77]. This technique is corresponding to the synthesis of a compound that otherwise was not able to be prepared by direct synthetic procedure. Hence, there are several types of structural transformations, which are primarily influenced by the expansion of coordination numbers, thermal association, condensation, rearrangement of bonds, or the removal/exchange of solvents [64].

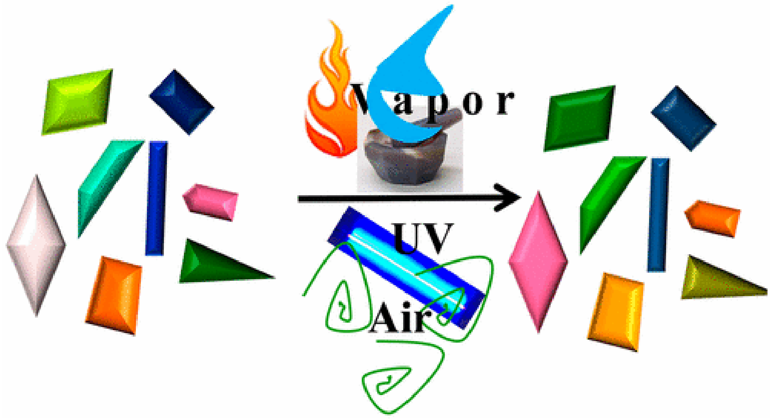


Figure 1.18: General schematic representation of SCSC transformation under external stimuli [77].

1.6 Luminescence studies

In 1888, the term luminescence was introduced by a German physicist, Eilhardt Weidemann. The word *lumen* is originated from the Latin word which mean light [78]. Since earliest times, luminescent phenomenon has drawn an interest to mankind in exploring its mysterious effects. The light prevailing luminescence naturally can be found in aurora borealis, glow worms, luminescent wood, rotting fish and meat [79]. In addition, the word 'phosphor' was derived from the Greek word that is corresponding to the luminescent materials known as a light carrier [80]. Luminescence is described as emission of light produced by absorption of energy like photons, electric current, chemical reactions, or a mechanical action which contains two basic types, namely fluorescence and phosphorescence [81,82]. The captivated of luminescent materials are not just focusing on lighting technologies only, but widely immense in several fields of research such as imaging, lasers, sensors and switches [83].

Coordination chemistry takes a lead part in contributing the luminescent probes from metal ions [84]. In recent years, a series of d^{10} metals like copper(I), silver(I), gold(I), zinc(II) and cadmium(II) complexes have aroused much attention due to their appealing structures, moreover these metals assemble good possess in luminescence properties [85]. Nonetheless, lanthanide ions are also been documented to receive excessive attention due to their superior emission and well performed in luminescence materials [86]. Luminescence can arise from direct organic ligands especially those highly conjugated, charge transfer such as metal-to-ligand charge transfer (MLCT) and also metal-centred emission as observed in lanthanide complexes through antenna effect [87]. It has been noticed that the metal complexes containing π-conjugated aromatic ligands were found to be highly luminescent especially for those incorporating with d^{10} elements and lanthanides ions, hence can be used as luminescence sensors and OLEDS [88-90]. Noteworthy, OLEDs have widely immersed in the chemistry field as well as engineering and physics over the last couple of decades because of their huge potential for the expansion of new technology in the solid-state lighting application and flat panel display [91].

The behavior of luminescence properties apparently related with the coordination environment of central metal ions and the surrounding ligands [92]. Recently, the luminescence properties of metal-organic frameworks (MOFs) have accepted great interest as well [81]. The interactions between metal ligand used in designing coordination polymers and MOFs allow the energy transfer processes between the organic and inorganic part, which then can be used to tune luminescence processes and their efficiency [93]. Among others, photoluminescence is one of a common luminescence that describes as emission of photons by electromagnetic radiation through ultraviolet, visible light and infrared radiation [94].

Kan *et al.* reported the photoluminescence studies for numerous highly connected MOFs based on d^{10} metals. One of the example is a 3-D net based on heptanuclear Ag_7 core, $[Ag_7(4,4'\text{-tmbpt})(HL)_2(L)(H_2O)]_n$, (where 4,4′-tmbpt = 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole and L = 5-(4-carboxybenzyloxy)isophthalic acid), prepared via hydrothermal synthesis (Figure 1.19) [95]. Remarkably, in that reported work, the emission peak of this coordination polymer complex was highly red shifted (higher wavelength) probably due to the changes of organic ligands in their HOMO and LUMO energy levels after the coordination to metal centres. Moreover, the formation of red shifted band could also due to the charge transfer between the organic ligands and metal centres [95].

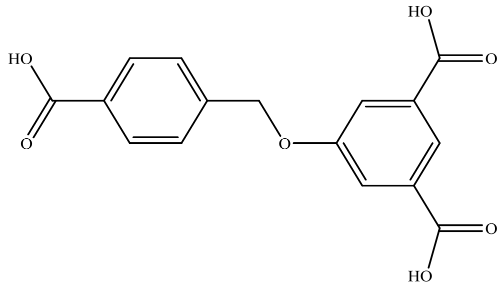


Figure 1.19: Structure of 5-(4-carboxybenzyloxy)isophthalic acid (H_3L) that was used along with co-ligand, 4-4'-tmbpt to facilitate the formation of 3-D net structure.

Besides, Subri *et al.* also reported the formation of $[Ag_2(tdza)(PPh_3)_2)]_n$ that possesses a 2D polymeric structure, afforded by synthesis reaction of flexible dicarboxylate ligand, (1,3,4-thiazole-2,5-diyldithio)diacetic acid (H_2tdza) with silver(I) and triphenylphosphine (PPh_3) (Figure 1.20). The complex $[Ag_2(tdza)(PPh_3)_2)]_n$ features the potential luminescence material with the emission peak at 499 nm (Figure 1.21), indicates blue shift (lower wavelength) of emission maxima considerable from metal ligand charge transfer (MLCT) [96].