

## **Summary**

Organic-inorganic hybrid solids form an interesting class of solids owing to their intriguing properties and applications. It is certain that hybrid solids can revolutionize current technological and scientific world. Therefore, in this chapter, a general introduction to organic-inorganic hybrid solids has been provided, along with an overview on different types of hybrid solids based on polyoxometalates and transition metals. In addition, the applications of these solids in diverse fields have also been included. The chapter also provides an insight on the various synthetic methods employed for preparing hybrid solids. Finally, the motivation and objectives of the present research work have been highlighted towards the end of the chapter.

## **I. Introduction**

Man's quest for survival and his inherent curiosity enkindles many to delve into the mysteries of matter. Right from the Alchemists, it has resulted in continuing human attempts to explore, create and make use of materials that possess unique and novel properties. However, it often takes a lot of endeavours to gain in-depth knowledge and understanding of the hidden characteristics and potentials of such materials.

The field of *Hybrid Solids* is one such area where the scientific community still strive hard to fully understand the chemistry of formation, to create innovative combinations and to explore the possible applications.

### **I.1 Hybrid solids**

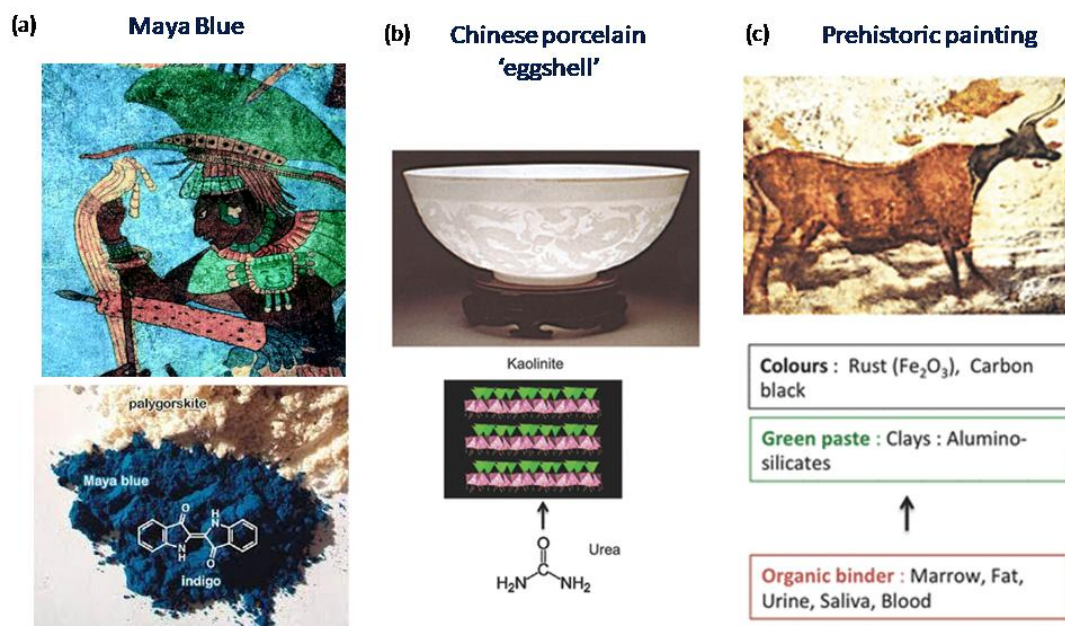
Hybrid solids, constituting both organic and inorganic components, represent an interesting class of materials due to its structural versatility and diverse applications [1-3]. According to the International Union of Pure and Applied Chemistry (IUPAC), a hybrid solid is defined as "Material composed of an intimate mixture of "inorganic" components, "organic" components, or both types of components. Note: The components usually interpenetrate on scales of less than 1 $\mu$ m" [4]. Hybrid solids are not just a physical mixture; rather it's a creative blend of organics and inorganics, incorporating the properties of both components [5,6]. The organic part provides the structural diversity, tunability and flexibility whereas rigidity and thermal stability is given by the inorganic components [7]. Such tailored solids not only combines the characteristics of the building blocks but can also present unusual and/or improved properties acquired from the interaction of both [8].

### **I.1.1 Hybrid Solids: Historical Perspective**

The concept of hybridisation in developing hybrid solids is not just man's merit; rather it is the basis of evolution. Materials like mollusc shells or crustacean carapaces, bone or tooth tissues in vertebrates, are all naturally occurring integrated hybrid systems [9]

The mixing of organic and inorganic components was carried out in ancient world. Novel mixtures of dyes or inorganic pigments were used in mural paintings thousands of years ago. The colourful pigment Maya Blue is a very good example for a hybrid material used by the Mayan people around 6<sup>th</sup> century AD, which was prepared by mixing of natural dye "indigo" and "palygorskite", a natural fibrous and microporous clay[10]. This hybrid showed improved colour fastness, thermal and chemical stability compared to the pure components [11]. Chinese rice – lime mortars developed by mixing sticky rice soup with lime and other standard mortar ingredients were used in ancient China around 1500 years ago [12]. Amylopectin from the sticky rice organic component bound with the inorganic components such as clay minerals, calcium carbonate, and sand (silica) resulted in mechanically stable hybrids used for construction of tombs and sections of the Great Wall during the Ming dynasty [13]. Many other clay – organics were used worldwide in various fields like cosmetics and medicine [14].

However, the field of research on hybrid solids was more developed by the end of the 20th and the beginning of the 21st century, because of the availability of modern physico–chemical characterization methods, which gives a deep insight into the hybrid architectures [15]. Since then, 'hybrid solids' has become a mushrooming multidisciplinary research area driven by the curiosity of scientists from all fields of science.



**Figure I.1** A few examples of hybrid materials used in ancient world; (a) Maya blue [10], (b) Chinese porcelain [2] and (c) pre-historic paintings [2].

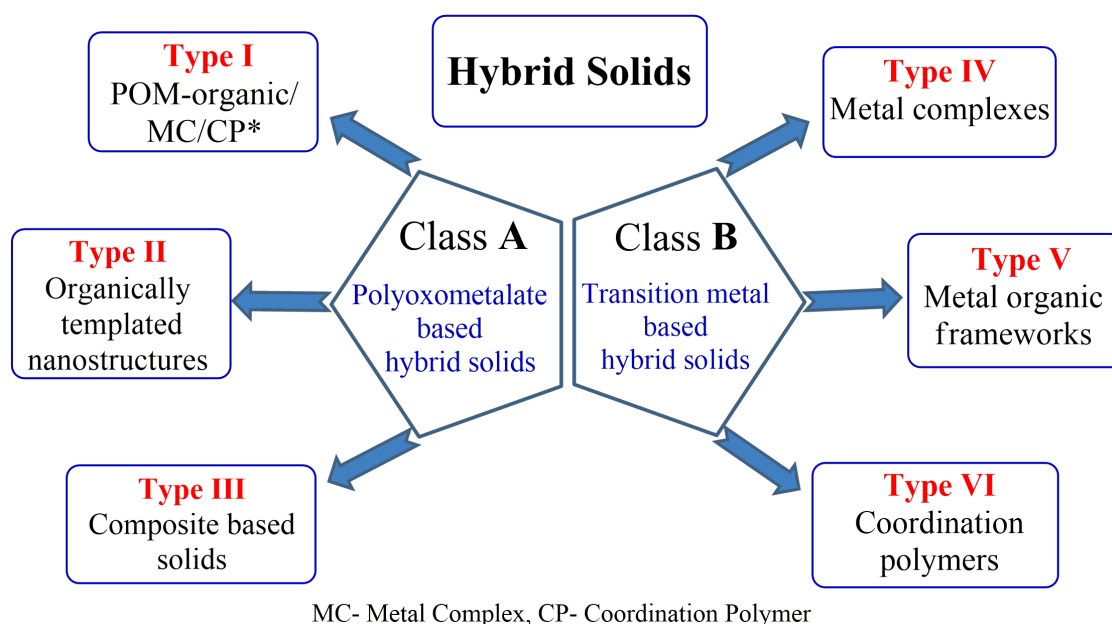
## I.2 Classification of Hybrid Solids

The term 'hybrid solid' spans over a wide variety of materials ranging from simple metal complexes to crystalline highly ordered coordination polymers and metal organic frameworks, metal-oxo clusters, amorphous sol – gel compounds, nanocomposites and several other solids with and without interactions between the inorganic and organic units. Different authors categorise hybrid solids in various ways, making it a very subjective process. The nature of interaction between the organic and inorganic components plays a significant role in controlling the physical and chemical properties. Sanchez *et.al.* has classified hybrid solids into two main classes depending on the strength of interaction between the components [16];

Class I - Hybrid solids which are formed through weak interactions like Vander Waals interaction, hydrogen bonding or weak electrostatic interactions, between the organic and inorganic components.

Class II- Hybrid solids that are formed through strong chemical interactions in which the components are linked by covalent or ionic-covalent chemical bonds.

In this thesis, we have classified hybrid solids into two main classes based on the nature of the inorganic building blocks. Class A belongs to hybrid solids based on polyoxometalates (POMs) whereas Class B consists of hybrid solids based on transition metals. Scheme I.1 shows the various types of class A and class B hybrid solids.



**Scheme I.1** Different types of class A and class B hybrid solids

The work presented in this thesis is mainly focused on type I- type IV hybrid solids. Therefore, a brief explanation on POM hybrids with organic ligands/metal complexes or coordination polymers (type I), organically templated nanostructured POM hybrids (type II), composite-POM hybrids (type III) and transition metal complexes (type IV), are provided in the following sections.

### I.3 Polyoxometalate based hybrid solids (Class A)

Polyoxometalates (POMs) are a significant class of polynuclear anionic clusters, made up of transition metals in high oxidation state (usually of Mo, V, W, Ta, Nb, etc.) and oxygen atoms [17]. These POMs are well known for their rich topology and intriguing physical and chemical properties and hence have received immense attention [18]. The unique properties of POMs have made them promising candidates in the fields of catalysis [19-21], magnetism [22], medicine [23-27], sensors [28] and material science [29].

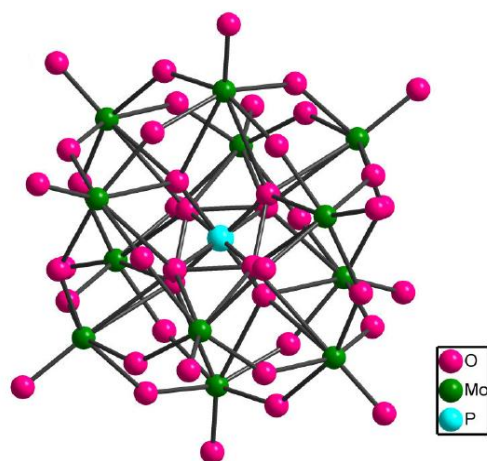
POMs are broadly classified into two types; isopolyanions with the general formula  $[\text{H}_x\text{M}_y\text{O}_z]^{n-}$  which lack heteroatoms and heteropolyanions  $[\text{X}_x\text{M}_m\text{O}_y]^{q-}$ , X = heteroatom, usually a first row transition metal) that contains one or more heteroatoms in the metal-oxide framework [30]. The presence of heteroatoms can bring about a great structural variety of POM solids which includes Keggin  $[\text{XM}_{12}\text{O}_{40}]^{n-}$  [31], Wells-Dawson  $[\text{XM}_{18}\text{O}_{62}]^{n-}$  [32], Strandberg  $[\text{XM}_5\text{O}_{23}]^{n-}$  [33] and Anderson-Evans archetypes  $[\text{XM}_6\text{O}_{24}]^{n-}$  [34,35].

In this work, hybrid solids based on Keggin type and Anderson-Evans type POMs have been synthesized and therefore, a brief structural description of these two types are discussed below.

#### I.3.1 Keggin type cluster, $[\text{XM}_{12}\text{O}_{40}]^{n-}$

Keggin type POM cluster,  $[\text{XM}_{12}\text{O}_{40}]^{n-}$  was first structurally determined by Keggin in 1933 [31]. It consists of a central  $\text{XO}_4$  tetrahedra surrounded by 12 $\text{MO}_6$  (M = Mo or V) octahedra arranged in four groups of three edge– shared octahedral,  $\text{M}_3\text{O}_{13}$ . The common site of  $\text{M}_3\text{O}_{13}$  is also linked to the central heteroatom X. Baker and Figgis have reported five geometrical isomers of Keggin ion, of which the  $\alpha$  isomer being the more

predominant and thermodynamically stable [36]. The structure of  $\text{PW}_{12}\text{O}_{40}^{3-}$  studied by Keggin corresponds to  $\alpha$  form [31]. Rotation of one, two, three or all the four  $\text{M}_3\text{O}_{13}$  units by  $60^\circ$  give rise to  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$  isomers respectively. Keggin type cluster anions when treated with alkaline solutions result in the loss of one or more metal centres thereby forming lacunary Keggin POMs [37]. The vacant sites can then be filled by suitable transition metal ions forming substituted Keggin clusters [38,39].

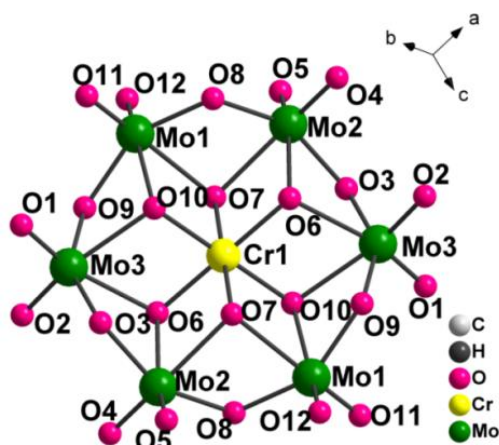


**Figure I.2** Structure of Keggin type POM.

### I.3.2 Anderson-Evans type cluster, $[\text{XM}_6\text{O}_{24}]^{n-}$

Anderson-Evans type is one of the most common POM clusters having the general formula  $[\text{H}_x(\text{XO}_6)\text{M}_6\text{O}_{18}]^{(9-x)-}$ , where  $x = 6-7$ ,  $\text{M} =$  addenda atoms ( $\text{Mo}^{\text{VI}}$ ) and  $\text{X} =$  a central heteroatom [40]. The structure of Anderson-type POMs was first suggested by J. S. Anderson [34] in 1937 and later confirmed by H. T. Evans [35]. It consists of six edge sharing  $[\text{MoO}_6]$  or  $[\text{WO}_6]$  octahedra arranged in a hexagonal manner around the central  $[\text{XO}_6]$  octahedron resulting in a planar structure of  $\text{D}_{3d}$  symmetry [35]. The oxygen atoms present in the Anderson cluster exhibits three different types of coordination modes; six triple-bridged oxygen atoms ( $\mu_3\text{-O}$ ) connecting the two adjacent addenda atoms and the central heteroatom, six double-bridged oxygen atoms ( $\mu_2\text{-O}$ ) connecting two addenda atoms and two terminal oxygen atoms ( $\text{O}_t$ ) linking to each of the six addenda atoms

(Figure I.3). The Anderson POM can be generally classified into two types; A-type Anderson in which all six  $\mu_3$ -O atoms are unprotonated with the general formula  $[X^{n+}M_6O_{24}]^{(12-n)-}$  (the central heteroatom is usually in a high oxidation state, for example,  $X = Te^{VI}, I^{VII}$ ) [41,42] and B-type Anderson in which the  $\mu_3$ -O atoms are protonated with the general formula  $[X^{n+}(OH)_6M_6O_{18}]^{(6-n)-}$  (heteroatoms usually in low oxidation state, for example,  $X = Cr^{III}, Fe^{III}$ ) [43,44].



**Figure I.3** Structural unit of Anderson-Evans cluster anion

### *Designing POM cluster hybrids*

#### **I.3.3 POM-organic ligands/MC/CP hybrids (Type I)**

POM anionic clusters possess counter cations other than inorganic ions as well. POMs can frequently interact with transition metal complexes, coordination polymers, or organic ligands via self-assembly approach thereby increasing its structural diversity and thus resulting in novel POM cluster based hybrid solids [45,46]. Hence, the design and synthesis of such hybrids, which result from the incorporation of organic moieties into the metal oxide framework, have received a lot of interest. Several well-defined POM-based hybrid solids, including the Keggin [47,48], Wells-Dawson [49,50] and Lindquist kinds [51,52], have been reported. Anderson type POMs with its planar geometry are ideal



inorganic building blocks and have been explored by many groups to synthesize Anderson cluster based hybrid solids with metal-organic complex or coordination polymers [53-57]. It can form hybrids in which Anderson-Evans cluster occurs as discrete anion and metal-organic complex or coordination polymer occurs as counter cation as in  $[\{M_2(2\text{-pzc})_2(\text{H}_2\text{O})_4\}\{\text{CrMo}_6(\text{OH})_7\text{O}_{17}\}]_3 \cdot 17\text{H}_2\text{O}$  ( $M = \text{Co}$  or  $\text{Cu}$ , 2-pzc = Pyrazine-2-carboxylate) and assembled through non-covalent interactions [58]. On the other hand, in some cases, Anderson cluster is coordinated to metal-organic complex or coordination polymers which are further extended to form 1-D chains, 2-D sheets, or 3-D frameworks. For example, Shivaiah *et.al.* reported a novel POM hybrid comprised of Anderson cluster anion and a coordination polymer  $\{[\text{Cu}^{\text{II}}(2,2'\text{-bipy})(\text{H}_2\text{O})_2\text{Cl}][\text{Cu}^{\text{II}}(2,2'\text{-bipy})(\text{H}_2\text{O})_2\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 4\text{H}_2\text{O}\}$ , which was the first example of an extended spiral chain hybrid structure [59]. Pavani *et. al.* has synthesized three new extended Anderson hybrids viz;  $[\{\text{Cu}_2(\text{ox})(\text{pz})_4\}\{\text{H}_7\text{CrMo}_6\text{O}_{24}\}]\cdot 11\text{H}_2\text{O}$ ,  $[\{\text{Cu}(\text{pz})_2(\text{H}_2\text{O})_2\}\{\text{Cu}_2(\text{ox})(\text{pz})_4\}\{\text{H}_5\text{CrMo}_6\text{O}_{24}\}]\cdot 8\text{H}_2\text{O}$  and  $[\{\text{Cu}(\text{pz})_3\text{Cl}\}\{\text{Cu}_2(\text{ox})(\text{pz})_4\}\{\text{H}_6\text{CrMo}_6\text{O}_{24}\}]\cdot 8\text{H}_2\text{O}$  in which the Anderson cluster is covalently linked into 1-D chain and 2-D sheets via oxalate(*ox*) bridged copper pyrazole (*pz*) units [60]. Organic ligands also can serve as counter cations to POM anionic clusters which can assemble through supramolecular interactions as in  $(\text{H}_2\text{pip})_5[\text{AlMo}_6(\text{OH})_6\text{O}_{18}]_2(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$  [61]. Anderson type chromium molybdates with organic cations reported in literature has been summarized in Table II.1 of chapter II.

### **Applications:**

POM cluster hybrids not only exhibit diverse architectures but also interesting properties and hence, a wide range of promising applications especially in the field of catalysis, photochromism, material science and medicine [62,63].

The presence of terminal oxygen atoms in POMs contributes to high reactivity and therefore, POM clusters with varying counter ions are studied for their catalytic properties in a variety of reactions. For instance, Peng *et.al.* isolated a new Anderson hybrid  $(\text{H}_3\text{O})[(3\text{-C}_5\text{H}_7\text{N}_2)_2(\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18})]\cdot 3\text{H}_2\text{O}$  ( $3\text{-C}_5\text{H}_6\text{N}_2 = 3\text{-aminopyridine}$ ), and found to possess good catalytic oxidation activity for eliminating acetone at lower temperature [64]. Wang's group has reported a Keggin type POM hybrid templated by a coordination polymer,  $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{bpp})_2\text{Cl}][\text{PM}_{12}\text{O}_{40}]\cdot \sim 20\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}$ ;  $\text{bpp} = 1,3\text{-bis}(4\text{-pyridyl})\text{propane}$ ) which exhibited significant electrocatalytic activity towards the reduction of nitrite [65].

POMs combined with organic amines,  $\pi$ -conjugated molecules or polymers can form hybrid solids with enhanced photochromic properties. For instance,  $(\text{H}_2\text{DABCO})_2(\text{NH}_4)_2[\text{Mo}_7\text{O}_{24}]$  was found to exhibit photochromic behavior upon UV excitation together with trimolybdate and octamolybdate derivatives as reported by Coué *et. al.* [66]. Recently, Liu *et.al.* prepared a polyoxomolybdate-naphthalenediimide hybrid,  $[\text{Ce}_2(\text{BINDI})(\text{DMF})_8]\cdot [\text{Mo}_6\text{O}_{19}]$ , ( $\text{BINDI} = N, N'\text{-bis}(5\text{-isophthalic acid})\text{-}1,4,5,8\text{-naphthalene diimide}$ ), which showed reversible photochromic behavior under uv-visible light irradiation. It also showed good photocatalytic activity for degradation of methylene blue under visible light [67].

POMs can also form biologically active hybrid materials and hence show potential applications in medicine. Anderson type solid,  $[\text{NH}_3\text{Pr}^i]_6[\text{Mo}_7\text{O}_{24}]\cdot 3\text{H}_2\text{O}$  was tested *in vivo* against various tumor cell lines and exhibited potential antitumor activity [68]. A series of novel pyridinium polyoxometalates synthesized by Wang and co-workers are reported to have good anti-HIV-1 activities [69].

Apart from above fields, POM hybrids are also explored for their potential applications in macromolecular crystallography studies and magnetism [70]. The synthesis of POM

cluster based hybrids continues to fascinate the researchers owing to its interesting properties and versatile applications.

### **I.3.4 Organically templated nanostructured POM hybrids (Type II)**

Nanostructured POMs templated by organic moieties such as organic amines, proteins, surfactants, etc. constitute another prominent type of hybrid solids [71-73]. These nanostructures are self-assembled via supramolecular interactions and are much less ordered. The type of organic template used has a significant impact on the morphology and properties of the hybrid formed, in addition to other synthetic variables like pH, reactant quantity, temperature, etc. Long chain amines have been used for synthesizing nanostructured vanadium and molybdenum oxides by using soft chemistry routes [74-77]. Spahr *et. al.* isolated a lamellar type vanadium oxide hybrid templated by hexadecylamine having nanotubular morphology. The tunnel apertures were between 5 and 50 nm, and the tube diameters varied from 15 to 100 nm [74]. Molybdenum oxide nanofibres were synthesized by intercalation of primary amines into layers of MoO<sub>3</sub> with diameters ranging from 50-150 nm, as reported by Niederberger *et. al.* [75]. The introduction of surfactants as unique counter cations offers a feasible way of creating nanostructured POM hybrids. Surfactant encapsulated clusters are formed from a solution containing reduced POM species [78]. On the other hand, surfactants intercalated into POM framework tend to form chains and sheets, if the solution contains only the oxidized POM species [76,79]. Thomas *et.al* have investigated the growth of phosphomolybdate solids templated by dodecylpyridinium cations (DPC) under acidic conditions, and resulted in nano rods of high aspect ratio [80]. Keggin type polyoxometalate nanorods were prepared using polyethylene glycol (PEG) surfactant as a template by Yang *et. al.*[81].

**Applications:**

Nanostructured POM hybrids show promising applications as catalysts, pH probes, photochromic/electrochromic materials and as adsorbents for dye removal [82-85].

Peroxo polytungstophosphates (P:W = 1:4) prepared using Aliquat 336 as a surfactant showed good catalytic activity towards epoxidation of propylene [82]. Wang and co-workers have fabricated multilayer films consisting of  $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]$  ( $\text{EuW}_{10}$ ) templated by dimethyldioctadecylammonium chloride (DODA) which exhibited photoluminescence [84]. Surfactant encapsulated nanospherical polyoxometalate, ( $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ ) was found to exhibit remarkable anionic dye removal activity [85]. Organic functionalities are particularly intriguing for bioactive POMs because they improve the POMs' association with biologically significant targets as well as their stability in specific media. Nanorods of amino acid – phosphomolybdates synthesized using reverse micelles as a template showed potential antibacterial activity against *Escherichia coli* than the individual components [86]. Such a remarkable activity could be primarily attributed to the nano-size effect.

The use of organic templates in forming nanostructured POMs has led to the expression of synergistic functionality and diverse applications in POM hybrid materials.

**I.3.5 Composite based POM hybrids (Type III)**

Composite based POM hybrids have gained increased attention in recent years because of their multifaceted architectures, superb redox activities, and exceptional proton and electron transport capabilities. POMs can form composites with conducting polymers, graphene, carbon nanotubes (CNTs), and metal nanoparticles (NPs) resulting in hybrid materials of improved stability and interesting properties [87-90]. Several studies have shown that embedding POMs into polymers can be used to control the nanoscale

aggregation behaviour of the hybrids which in turn can affect the final properties [91,92]. Among the various polyoxometalates, Keggin and Dawson type POMs are widely used for preparing composite based hybrid solids. Cuentas-Gallegos *et al.* prepared a novel composite using Keggin type POMs and functionalized CNTs [93]. Dawson type phosphotungstate-graphene oxide composites were synthesized by Wang *et al.* [94]. A Keggin-type POM,  $H_3PMo_{12}O_{40}.nH_2O$ , that can be used as a potent oxidising agent to polymerize pyrrole and form composite material has been reported by Gomez-Romero and Lira-Cantu [95].

### ***Applications:***

Composite based POM hybrids find promising applications in various fields such as photocatalysis [94], as sensors [96], supercapacitors [93] and energy storage devices [97]. A few of such applications are discussed below.

Keggin-type POM modified Ag/Graphene composite materials synthesized by Li *et al.* displayed excellent activity and stability for electrocatalytic oxidation of water under neutral conditions [98]. Ammam and Easton prepared a Dawson type POM-Polypyrrole composite which exhibited remarkable sensing activity towards  $NO_x$  gases [96]. Polyaniline (PANI), a conducting polymer, has been combined with Keggin POMs to form composites for supercapacitor applications [99,100]. A novel POM hybrid,  $[(C_4H_9)_4N]_3[PMo_{12}O_{40}]$  and graphene composite, was reported to be an advanced cathode material for high performance lithium ion batteries (LIBs) [101]. Another Keggin type SiW<sub>12</sub>/rGO nanocomposite as a cathode material for LIBs has been reported by Wang *et al.* [102]. POMs have also been combined with naturally occurring polymers such as chitosan, which showed enhanced thermal stability and mechanical properties [103] and were also found to possess good antimicrobial activity [104]. A review of

phosphomolybdate-polymer composites and its applications, reported in the last decade, has been summarized in Table VI.1 in chapter VI.

## **I.4 Transition metal based hybrids (Class B)**

### **I.4.1 Metal complexes (Type IV)**

Metal complexes, comprising of transition metal atoms/ions and organic ligands linked via coordination bonds, are an intriguing class of organic-inorganic hybrid solids. The topology and properties of these hybrid solids can be tailored through judicious choice of their molecular building blocks. There are two main building blocks used for forming metal complex viz; metal ions and organic ligands.

Among the various metal ions, transition metal ions are widely used for the construction of metal complexes since they can exhibit variable oxidation state and diverse coordination geometries. For example, Cu(II) exhibits Jahn-Teller distortion and usually form distorted octahedral or distorted tetrahedral or square planar geometries. Co(II) usually prefers octahedral geometry, however, in strong acidic solutions it adopts tetrahedral form. Ni(II) and Pt(II) generally tends to form square planar geometry. Various metal ions also form other geometries like linear, trigonal planar, square pyramidal, etc.

Organic ligands are coordinated to the metal centre via the donor atoms, usually, N, S and O atoms. It can be either monodentate or multidentate for effective coordination to the metal centre. Ligand molecules also differ in their charges, being neutral or anionic. The shape of the ligand and other functionalities such as presence of aromatic rings, heteroatoms, chirality, etc. also plays crucial role in tuning the properties of the metal-complex hybrid. Heterocyclic compounds, especially N-containing heterocyclic ligands such as pyridines, pyrazines, pyrazoles, etc. are ideal moieties for coordinating with the

metal ions as they possess interesting properties [105, 106]. Besides the metal ions and organic ligands, solvent molecules also play a role in the formation of metal complex, either by coordinating with the metal centre or as co-crystals.

***Applications:***

Transition metal complexes (TMCs) are well-known for their potential applications in various fields including medicine [107], catalysis [108], solar energy conversion [109], magnetism [110], etc. A vast number of studies of TMCs are based on their potential to be used as antimicrobial, antitumor, antiviral, antioxidant and antidiabetic agents. A novel triazene based Ni(II), Co(II), Cu(II) and Zn(II) complexes were reported to exhibit promising antidiabetic and antioxidant activity [111]. Saha *et.al.* synthesized a Cobalt complex with histidine that displayed significant antibacterial and antifungal activity against various multidrug resistant bacterial and fungal strains in comparison to commercial antibiotics [112]. A series of Cu, Zn and Cd complexes based on 2-acetylpyridine and L-tryptophan were tested for anti-cancer activity on MDA-MB-231 breast cancer cells and the Cd complex showed the highest anti-proliferative activity among the three complexes as reported by Zhang *et. al.*[113].

TMCs are studied for their catalytic properties in various reactions such as polymerization, oxidation of organic compounds, reduction of thionyl chloride, etc.[108]. For example, Iron(III) and cobalt(II) complexes based on pyridine bis(imine) ligand showed significant catalytic activity for polymerization of ethylene [114]. A new Ru(II) carbonyl complex containing ‘pincer like’ ONS donor Schiff base and triphenylphosphine was prepared by Tamizh *et. al.* for selective oxidation of alcohols at room temperature [115].

TMCs have also been explored for efficient energy storage/conversion devices including dye sensitized solar cells [116], organic light emitting diodes [117] and in drug delivery

systems [118]. Several TMCs are also promising candidates as chromotropic materials [119-120]. A detailed review of chromotropism shown by complexes of Cu(II) tetrahalides with various organic ligands have been summarized in Table IV.1 in chapter IV.

## **I.5 Synthetic strategies**

Various synthetic methods generally employed for the synthesis of type I to type IV hybrid solids mentioned above are briefly discussed in this section.

### **I.5.1 Solvent evaporation method**

Solvent evaporation is one of the most commonly used methods for preparing POM hybrid solids and metal complexes. Reactants are dissolved in a suitable solvent and left undisturbed for crystallization, usually at room temperature. As the solution becomes saturated, either by cooling the solution or by evaporating extra solvent, crystals gradually develop. The obtained crystals are filtered, washed with water or other solvents and dried at room temperature.

### **I.5.2 Hydrothermal method**

Hydrothermal synthesis is another technique employed in the synthesis of a wide range of hybrid solids, especially if the organic moieties have poor solubility. The reactants along with water are added into a sealed Teflon container. The reaction is carried out under autogenous pressure at temperatures ranging from 100-250°C. The apparatus is allowed to undergo slow cooling and the product obtained is filtered, washed with water or other solvents and dried. This method is especially suitable for the growth of good-quality crystals required for single crystal analysis and offers more control over the composition of the hybrid formed.



### **I.5.3 Sol-gel method**

Sol-gel method is another technique particularly useful for the synthesis of organically templated nanoclusters and nanocomposites. The basis of this method is preparing a homogeneous sol from the molecular precursors and converting into a gel. The gel obtained is dried after removing the solvent by suitable methods. The sol-gel method is very useful for the preparation of highly homogeneous composites with very high purity.

Various other methods such as co-precipitation, layer diffusion, sonication, etc are also occasionally used for the synthesis of different types of hybrid solids.

### **I.6 Motivation**

Polyoxometalate hybrids and transition metal complex hybrid solids holds a prominent position among the wide range of organic-inorganic hybrid materials. They exhibit interesting properties and diverse applications as evident from the literature. POM clusters can form structurally diverse hybrid solids with organic ligands, metal complexes or coordination polymers. POMs can also form interesting nanostructures templated by organic moieties such as long chain amines, surfactants, etc. When POMs are combined with polymers or carbon nanotubes, it can result in the formation of nanocomposites. This structural versatility contributes to its potential applications in the area of catalysis, sensors, material science and medicine. Transition metal ions on interaction with organic ligands form metal complexes driven by metal-ligand coordination, which shows promising applications in various fields. In addition, hybrid solids of POMs and TMCs are also capable of exhibiting supramolecular interactions such as H-bonding, C-H $\cdots$  $\pi$ ,  $\pi\cdots\pi$  interactions, etc. that can provide extra stability to the crystal structure. However, varying the reaction parameters such as pH, temperature, nature of the metal ions, nature of the organic ligands, solvents, etc. exert a strong influence on the self-assembly process of hybrid solids.

In this context, synthesis of structurally diverse hybrid solids and investigating its properties, by varying the synthetic parameters, seems to be an interesting area of research. The study of various supramolecular interactions that dictate the self-assembly process can also throw light on the properties of hybrid solids.

## **I.7 Objectives**

Based on the above observations, the major objectives of this thesis are,

- Synthesize Polyoxometalate (POM) hybrid solids based on Mo; to exploit its linking propensity with transition metal ions and heterocyclic organic ligands like Pyrazole and 2- aminopyrazine.
- Explore the role of supramolecular interactions such as hydrogen bonding, C-H $\cdots$  $\pi$ ,  $\pi\cdots\pi$  interactions, etc. in the crystal packing of the hybrid solids.
- Investigate the phenomenon of ‘chromotropism’ in aminopyridine based copper tetrahalides.
- Explore the biological activities of selected synthesized solids.
- Investigate the effect of long chain surfactants on the composition and morphology of phosphomolybdate solids and its application in dye removal.
- Synthesize ammonium phosphomolybdate-polypyrrole composite and investigate the effect of synthetic parameters and properties.

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