Predominantly ligand guided non-covalently linked assemblies of inorganic complexes and guest inclusions

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Abstract. Various non-covalently linked inorganic self-assemblies formed by the supramolecular interacting sites located at the ligands are discussed. The impetus for this rapidly growing topic on the construction of robust assemblies is elucidated by select examples that are associated with interesting structures and properties. The review includes discussion on the stabilization of different assemblies of nucleobases in the non-covalent assemblies of inorganic complexes. The participation of the guest molecules in the formation of self-assemblies with hosts to make extra space or voids for intake of the guest, water-assisted assemblies, changes in the structures guided by cations, and aggregation-induced photoluminescence in the self-assemblies of metal complexes are presented. Fine-tuning of non-covalent self-assemblies of metal complexes by changing ligands or by other components, which modify the guest recognition abilities is elucidated. The discussions are based on selected examples of self-assemblies that use supramolecular features of peripheral part of ligands or ligand of a complex that helps one to identify templates for weak interactions and for molecular recognition.

Keywords. Inorganic complex; host–guest complex; molecular recognition; non-covalent interaction; self-assembly; supramolecular assembly.

1. Introduction

Stability as well as physical properties of non-covalently linked self-assemblies are collectively decided by weak interactions within them.^{1,2} Preliminary ideas on the primary interactions between the host and guest molecules help to choose the correct combination for preparation of host–guest complexes. For a complete understanding of self-assemblies of host–guest complexes, one has to consider different types of interactions existing between host and host, host and guest as well as guest and guest.^{3–7} On the other hand, a study on surface inclusion compounds with low activation energy barrier of 1.2–9 kcal/mol is useful to understand and control the directional molecular motions associated with those materials.⁸ Hosts and guests molecules may independently self-assemble in several ways such as the ones outlined in Figure 1. These self-assembling processes may be through, (a) formation of porous stable architecture to accommodate guests;^{9–12} (b) reorganization of originally non-porous self-assemblies of host molecules to hold guest

molecules;^{13,14} (c) formation of self-assembly to provide hydrophobic or hydrophilic pockets of host molecules to accommodate guest molecules/ions as found in clathrates and water/ion clusters;^{15–22} (d) self-assembling between host and guest molecules to provide extra space for guests;^{23,24} (e) partial modification of self-assemblies of a host–guest complex to accommodate more/new guest molecules;²⁵ (f) forming dendrimer-like assemblies to include guest molecules.^{26,27} These organized self-assembling processes are commonly used to achieve effective guest binding in non-covalently linked assemblies. The directional properties, stability, physical properties of these assemblies are essentially guided by overall impact of weak repulsive as well as attractive interactions among the components of each self-assembly. Besides conventional host–guest complexes, there are non-covalently linked assemblies containing voids where another chemical species gets encapsulated. These are called inclusion compounds where such voids or channels are occupied by guests.^{28,29} Self-assemblies of certain compounds have intrinsic voids³⁰ and rest are self-assembled supramolecular assemblies originating from non-porous self-assemblies executing the performance similar to

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Figure 1. Schemes to modulate amounts of guest molecules in host-guest complexes.

porous structures by accommodating guests.³¹ In general, porous architectures with anions, cations and neutral molecules are less stable. Porous self-assemblies, often known as desolvates, are formed by loss of solvent of crystallization or guest molecules.

Host-guest chemistry through non-covalent interactions has grown rapidly over the years^{32–39} but systematic reports on non-covalently linked small inorganic complexes are relatively few.^{40–45} Coordination complexes having hydrogen bond donors or acceptors at peripheral sites are useful to design network structures.^{46,47} The π -stacking effect is realized as a major factor contributing to stability and physico-chemical properties of many self-assemblies.^{48–53} There are more hurdles to understand self-assemblies of inorganic complexes as metal ions bring versatility and complications through directional coordination, oxidation states, etc. The metal complexes with ligands are generally prepared in solution and solvent gets incorporated to ligand or crystallizes as a solvent of crystallization. Hence, the ability of an inorganic complex to accommodate solvent molecules of crystallization in lattice influences the architecture of self-assemblies.^{54–58} Increase in uptake of guest molecules in a self-assembly of the host is important to develop storage and delivery systems and in energy conversions. This aspect is

routinely studied by changing the porosity of metal-organic frameworks.⁵⁹ Inorganic chemists routinely use coordination polymers and metal-organic frameworks. But the self-assembling of coordination complexes through the peripheral effects of ligand to provide directional properties and different self-assemblies depicted in the Figure 1 warrant preparation of new supramolecular assemblies for advanced material properties. There are also definite concerns to evaluate properties of self-assembled inorganic complexes at the molecular level; such as, epitaxial growth of crystals in a controlled manner, self-assembled materials for future use as core-shell crystalline materials, and for neat bottom-up crystallization processes.⁶⁰ The subject of self-assemblies of host-guest complexes is very large, hence certain intrinsic characteristic features which primarily control weak interactions are essential for the logical design of a self-assembly. Among such intrinsic features, C–H... π interactions^{61,62} and π – π interactions^{63,64} contribute significantly to the respective packing patterns. Hierarchies of energies of different π -interactions^{65,66} are in general lower than strong or medium hydrogen bonds; yet, directional nature of these interaction makes indispensable contribution. Each self-assembling processes depicted in Figure 1 may have such contributions which

Figure 2. One-dimensional self-assemblies of nickel(II) 2,2'-biimidazolate complexes with different ancillary ligands.

necessitate one to understand their roles in conferring special features to physical and chemical properties of self-assemblies and host–guest systems. The implications of weak interactions in host–guest assemblies in chosen examples of mono- to tetra-nuclear inorganic complexes are discussed here. This article deals with a discussion on the non-covalently linked inorganic self-assemblies guided by the supramolecular features of the peripheral part of a ligand acting as a supramolecular template for host–guest inorganic complexes.

2. Non-covalently linked self-assemblies of inorganic complexes

Metal coordination and hydrogen bonds are routine parameters that influence self-organization of inorganic molecular crystals. Information on these two aspects as well as information on the lower hierarchical weak interactions helps to explain properties of such assemblies. As in the case of hydrogen-bonded organic self-assemblies, the conventional supramolecular self-assemblies of inorganic complexes are also formed by hydrogen bonds among the complexes. In self-assemblies of inorganic complexes, metal-metal interactions or π -metal interactions often come across as influencing factors in packing patterns. Self-assemblies of 2,2'-biimidazolate metal complexes possess extensive hydrogen

bonds to generate different types of superstructures depending on the status of the central metal ion, nature of counter ions, and ancillary ligands.⁶⁷ Due to the directional nature of hydrogen bonds, the hydrogen bonded self-assemblies of 4,4'-biimidazolate metal complexes⁶⁸ widely differ from the 2,2'-biimidazolate complexes. One-dimensional linear chains, zigzag ribbons, helical structures and 2-dimensional honey-comb sheets were found in various nickel(II) *tris*-2,2'-biimidazolate complexes upon variations of the hydrogen bond schemes by changing organo-ammonium cations.⁶⁷ The structures of a series of nickel(II) 2,2'-biimidazolate complexes were also modulated by changing the orientations of 2,2'-biimidazolate ligands in the coordination sphere. For example, one-dimensional hydrogen bonded self-assembly **1** was formed when two tertiary-butylpyridine ligands occupied the *trans*-coordination sites of a distorted octahedral geometry of the complex (Figure 2a). A zigzag hydrogen bonded one-dimensional self-assembly **2** was formed when a 2,2'-bipyridine ancillary ligand was used to satisfy the two coordination sites of nickel-2,2'-biimidazolate complex. Due to bidentate nature with a rigid geometry of the ligands, the 2,2'-bipyridine ligands occupy the *cis*-positions resulting in changes in the orientations of the 2,2'-biimidazolate ligands (Figure 2b) providing a one dimensional zigzag structure.

Metal complexes possessing suitably designed supramolecular features provide self-assemblies with interesting properties. For example, nicotinate anions held to

Figure 3. A water-assisted sheet-like hydrogen bonded self-assembly of *bis*-(2,2'-biimidazole)nickel(II) nicotinate dihydrate.

2,2'-biimidazole nickel(II) or cobalt(II) cationic complex anchor water molecules in crystal lattice (Figure 3). The carboxylate anions of the complex form hydrogen bonds with 2,2'-biimidazolate ligands. The water molecules present in the lattice knit the carboxylates to provide a sheet-like structure **3**.⁶⁹ Such water-assisted hydrogen-bonded assemblies undergo easy dehydration. In particular, the dehydration of such a silver complex under mild conditions was reversible; this was due to retaining the original backbone in the desolvate ensuring the reversible rehydration.

2,2'-Biimidazole containing metal complexes are versatile building blocks to construct a variety of architectures for inclusion complexes.⁷⁰ A striking feature of 2,2'-biimidazole silver complexes is the ability to form anion dependent self-assemblies differing in packing patterns. For example, silver complexes of different nuclearities are formed upon change of the anions of silver-2,2'-biimidazole complexes. Such differences originating from the number of silver atoms linked together influence the overall architecture of individual self-assembly by varying the number of hydrogen bonding sites per molecule.⁷¹ Self-assembly of cobalt(III) mixed ligand complex derived from 1,10-phenanthroline (phen) and 2,2'-biimidazole (*H₂biim*) with a composition $[\text{Co}(\text{phen})_2(\text{H}_2\text{biim})(\text{ClO}_4)_3 \cdot 0.5(\text{H}_2\text{O}_3)(\text{ClO}_4)]$ utilizes the N–H bonds of the 2,2'-biimidazole to bind with calf-thymus deoxyribonucleic acid (DNA). The complex gets anchored to DNA groove and it has binding constant $1.26 \times 10^4 \text{ M}^{-1}$. Due to such binding with DNA, cleavage of the DNA under photochemical conditions gets facilitated.⁷²

Cyanide is a highly polar ligand. When coordinated to a metal ion it acts as a good hydrogen bond acceptor. Accordingly, complex metal-cyanide ions participate in hydrogen

Figure 4. Self-assembly of hexacyanometallate with organocations.

bonding with organo-ammonium cations or solvents. For example, complex anions $[\text{M}(\text{CN})_4]^{2-}$ or $[\text{M}(\text{CN})_6]^{n-}$ (M = metal ion) possessing *bis*-amidinium cations form different hydrogen bonded molecular networks. One such assembly **4** is shown in Figure 4. Architectures of those assemblies depend on coordination geometry and coordination numbers of central metal ion. Number and location of hydrogen bonding sites on the cation dictate the directionality of such assemblies.⁷³

Cations in many complexes are derived by protonation in multiple nitrogen containing compounds. Such cations with favourable geometry act as hydrogen bond bridges form molecular networks. 4,4'-Bipyridinium and 4,4'-bipiperidinium ions are generally used to form molecular networks with $[\text{MCl}_4]^{2-}$ (M = Pd, Pt, Mn, Cd).^{74–78} Hybrid organic–organometallic as well as inorganic–organometallic non-covalently linked assemblies of such complexes with charge-assisted hydrogen bonds result in self-assemblies with different topologies. Many such assemblies are associated with interesting redox properties.⁷⁹ Anion guided porous self-assemblies of silver *bis*-pyrazole complexes are well known.⁸⁰

Urea-based metal complexes are well-known to provide hydrogen bonded self-assemblies. For example, *N,N'*-dimethylurea-cobalt complexes form one or two-dimensional hydrogen-bonded self-assemblies.⁸¹ Similarly, multifunctional ligands with hydrogen bonding sites such as metal complexes of lactic acid also form interesting self-assemblies. For example, self-assemblies of the zinc lactate complex of cation $[\text{Zn}(\text{metlc})(\text{Hmetlc})(\text{phen})]$ and anion $[\text{Zn}(\text{Hmetlc})(\text{phen})_2]$ [*Hmetlc* = methyl lactate mono-anion and *metlc* = methyl lactate di-anion] form three-dimensional hydrogen-bonded

Figure 5. A wheel and axle type self-assembled host.

open framework; where water molecules get encapsulated.⁸² Honeycomb-like porous network is formed by self-assembling of tris(bipyridyl-glycoluril)cobalt(III) chloride.⁸³ Shimizu and co-workers have reported the utility of simple yet interesting $[\text{Co}(\text{NH}_3)_6]^{3+}$ organosulfonates to form self-assembled structures with robust architecture wherein the triangular faces of the hexammine cobalt(III) complex provides sites for charge-assisted hydrogen-bonds.⁸⁴

From these selective examples, it is clear that interplay of weak interactions in coordination behaviour of metal ions are the prime factors in building non-covalent self-assemblies of inorganic complexes. Various possibilities to build multinuclear complexes, to introduce new the supramolecular sites with the aid of ligands, to use of mixed ligand complexes, utilizations of the cationic or anionic part of complexes to generate new self-assemblies are open-ended issues. Furthermore, conformational flexibility, the chirality of metal complexes or ligands are additional avenues for non-covalent assemblies for advanced materials.

2.1 Assemblies of chelated and macrocyclic ligand complexes

Metal chelates use the hydrogen bond donor/acceptor sites on the ligand or stacking interactions to self-assemble. Either of these interactions influences packing pattern and affect their physical properties. Self-assemblies formed by such complexes are guided by solvents, reaction conditions and the supramolecular features on the peripheral part of the ligands. The peripheral part effects π -stacks or stacks for tight packing which influence the physical and chemical properties of the complexes.

Due to the effectiveness of weak interactions in the solid state the mechanochemical syntheses are highly specific to generate interesting complexes. For example, chelate such as cobalt(II) dibenzoylmethanate dihydrate easily transforms to templates suitable for inclusion of guest molecules. Hexa-coordinated cobalt(II) dibenzoylmethanate having nicotin-imide ligands at two axial positions has a wheel and axle type structure. This structure helps the complex to serve as a template (Figure 5) to recognise different aromatic guest molecules.⁸⁵ Planar aromatic guest molecules are easily accommodated over the spaces over the self-assembled amide units.

A product formed through a solid phase synthesis may differ from synthesis through solution phase due to

Figure 6. Hydration vs. dimerization of mononuclear bis-malonate complex.

supramolecular interactions operational in the solid state more than in solution. For example, by variation of the reaction conditions, one may obtain a mononuclear or an aqua-bridged dinuclear cobalt 2-nitrobenzoate complex. Similarly, differences in products are observed upon manipulation of crystallization procedures/conditions. For example, crystallization from different solvents yield crystals of different polymorphs of aqua-bridged dinuclear cobalt 2-nitrobenzoate due to the different orientations of the nitro-groups.⁸⁶

There exist large numbers of self-assemblies of homometallic or heterometallic malonate complexes.^{87–89} Copper(II) malonate complexes with mononuclear and dinuclear blocks shown in Figure 6 are reported in the literature.⁹⁰ Cationic counterparts of those complexes control the thermal stability in the solid state. The preparation of a particular four coordinated square planar complexes is difficult as complication arises from hydration of the square planar complexes or from the propensity of square planar complexes to adopt square-pyramidal structures by dimerization as illustrated in Figure 6.

The energetic of *bis*-malonate metal complexes to get hydrated or to form dinuclear unit depends on the central metal ions. An energy calculation has shown that there is a 2.8 kcal/mol gain in energy to form dinuclear complex over hydrated copper(II) malonate complex; whereas such a gain in energy for the same process for cobalt(II) malonate complex is 3.5 kcal/mol; and it is 1.2 kcal/mol for nickel(II) malonate complex. In this regard, magnesium malonate is an exceptional case; in this case, the hydration energy and the energy required to form dinuclear complex from the corresponding mononuclear magnesium malonate complex are comparable. Thus, a synthetic procedure has to accommodate these minute differences affecting stabilities. Energetically, these effects are very small; hence they are generally competing with solute-solvent interactions and the energy supplied by the external or internal source while performing such reactions. Hence, the reaction conditions make an impact on the formation of a desired self-assembly.

Aluminium and gallium complexes having composition $[\text{M}(\text{dpp})_3]$ where $\text{M} = \text{Al}$ or Ga and $\text{Hdpp} = 1,3\text{-di(4-pyridyl)-1,3-propanedione}$ (Figure 7) are used as building

Figure 7. (a) Inclusion complex of metal β -diketonate complexes with toluene. (b) The complex $[Eu(Hdpp)_3(H_2dpp)]Cl_4 \cdot EtOH$.

Figure 8. π -Stacking contributing to self-assembly of metal complexes of 4-{4-[bis(2-pyridyl)aminomethyl]phenyl}-2,2':6',2''-terpyridine.

blocks for interpenetrated primitive cubic networks of mixed-metal-organic frameworks. They form inclusion complexes with toluene. Among 1,3-di(4-pyridyl)-1,3-propanedionate containing metal complexes, europium complex has zwitterion of $Hdpp$ ligand as well as a cationic H_2dpp ligand. This is an exceptional complex among the series of other complexes of $Hdpp$; it has a composition $[Eu(Hdpp)_3(H_2dpp)]Cl_4 \cdot EtOH$. In this complex, the partially protonated pyridyl groups form a hydrogen-bonded network.⁹¹

Self-assemblies of metal complexes $[M(bapt)Cl_2]$ ($M = Co^{2+}, Zn^{2+}$) of di-topic hybrid ligand 4-{4-[bis(2-pyridyl)aminomethyl]phenyl}-2,2':6',2''-terpyridine ($bapt$) has extensive π -stacking among the tripyridine unit⁹² (Figure 8). The ligand $bapt$ is an example of covalently linked 2,2':6',2''-terpyridine (tpy) and 2,2'-dipyridylamine (dpa) units. The lattice is primarily guided by the *face-to-face arene-arene* interactions and $C-H \cdots Cl$ interactions. The $C-H \cdots Cl$

interactions are between aromatic protons and coordinated chloride ions. The rings involved in *face-to-face arene-arene* interactions have centroid to centroid separations of rings as 3.5–3.7 Å. One set of pyridine rings has *edge to face* interactions contributing to the stability of the π -stacked structure. It is interesting to note that a $[Fe(bapt)_2](PF_6)_2$, one dpa site is protonated, that allows the change in electron-density in one of the pyridine unit. Dominant interactions in the packing pattern of this complex are *arene-arene* interactions and aromatic $C-H \cdots F$ hydrogen bonds. On the other hand, uncoordinated dpa participate in *edge-to-face* and *off-set face-to-face arene-arene* stacking interactions. These suggest that integrity of the original stacks of ligands remains upon the change of anions in such metal complexes, the reorganization in π -interactions caused by a change in the flexible dpa portion have little effect on the orientation of the less flexible tpy portion of the molecule.

Figure 9. The anion-dependent cocrystal having π -interaction among free ligand and coordinated ligand.

Anion and complexation influencing the π -stacking pattern of a ligand is clearly reflected in self-assemblies of dinuclear copper complexes $[\text{Cu}_2(\text{hmic})_3](\text{PF}_6)_4 \cdot \text{Hmic} \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{hmic})_3](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ in which ligand abbreviated as hmic is a condensate of hydrazine and 4-methylimidazole-5-carboxaldehyde.⁹³ Both these complexes have copper ions with square pyramidal geometry in cation $[\text{Cu}_2(\text{hmic})_3]^{4+}$ which is structurally centrosymmetric. Two ligands independently bind two copper ions and a third ligand acts as a bridge between two copper by complexing with each copper ion in bidentate fashion as shown in Figure 9. In $[\text{Cu}_2(\text{hmic})_3](\text{PF}_6)_4 \cdot \text{Hmic} \cdot 2\text{H}_2\text{O}$, the cation $[\text{Cu}_2(\text{hmic})_3]^{4+}$ is sandwiched between two free ligands one of which is from the neighboring molecule. The packing of hmic has parallel π -aromatic distances $\sim 3.6 \text{ \AA}$ where the stacking patterns have similarity to the coordinated ligand but such distances are less than $3.50 \text{ \AA}$ in the complexes. Such a stacking does not occur in $[\text{Cu}_2(\text{hmic})_3](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ as it is devoid of free ligand.

Ordered supramolecular arrays of various porphyrin derivatives are built by utilizing weak interactions.^{94–102} In a pre-organized environment, there is no scope for solvent reorganization hence primary electron reactions are fast even at very low temperature. Non-covalent self-assemblies have orderly arranged porphyrin units. These supramolecules have been studied as functional models of biological systems capable of inducing directional motion of electrons or excitation energy through hydrogen bonding. Each porphyrin is in a defined metallation state (metal or free base). The use of free base or metalloporphyrin building blocks enables the fabrication of arrays with predetermined metallation states. When mixing two complementary

porphyrin building blocks, the directed triple hydrogen bonding moiety makes it possible to form different kinds of multi-porphyrin supramolecules with different spatial relationships.

Covalently linked or non-covalently linked C_{60} unit to metal complexes were extensively reviewed along with their potential applications as light harvesting and advanced materials.^{103,104} C_{60} connected to β -diketoester unit **16** that has long hydrophobic chain hydrocarbon at one end and at other end has ammonium cation (as depicted in Figure 10), self-assembles with zinc-porphyrin complex having crown ether **15**.¹⁰¹ The ability of ammonium cation to bind with crown ether and zinc ion interacting with C_{60} generates a non-covalently linked assembly **17** in dichloromethane. Advantages of such non-covalent assemblies are due to the possibilities to tailor make by manipulation of reaction conditions. More recently, stable and soluble metal complexes with metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) of *salen*-type ligand namely (*N,N'*-ethylenebis(salicylimine)) functionalized with C_{60} are reported. These complexes are catalytically active for epoxidation reaction. The advantage of using these complexes as catalysts is that they can be transformed to the supported catalyst by introducing them into various sp^2 -carbon nanostructures, such as nanotubes and nano-fibres. The optical properties of the fullerene derivatives differ from the parent fullerene and depending on the central metal ion these complexes show strong absorptions in the region of 400–630 nm. The positions of such absorption are dictated by the nature of the transition metal ion. These non-covalent assemblies leave scopes to explore for their magnetic, electronic and photo-active properties.¹⁰⁵

Figure 10. Weak metal- π interactions and crown-ether-ammonium ion interactions in the self-assembly **17**.

The complex **18** has uracil groups attached to the periphery of porphyrin rings; these participate in hydrogen bonds with bis(decyl)melamine (**19**) to form cage-like architecture.¹⁰⁰ The hydrogen bonds between the host and guest is shown in Figure 11. Self-assembly of the porphyrin cages organizes as film of nano-meter thickness on mica surface. Decyl-hydrocarbon chains on the guest play as key players in organizing the molecules in the film. Upon formation of such assembly **20**, it turns-off the electronic communication between chromophores. The loss of communication due to aggregation causes decrease in the intensity of the UV-visible absorption.

Some of the porphyrin derivatives in solid state have microporous structures.¹⁰¹ Self-assemblies of hydrogen-bonded poly-functionalized porphyrins having less than eight hydrogen bonds do not generate robust porous solids. But utilizing stronger intermolecular interactions and adding more ligating sites such as carboxylates on the porphyrin periphery followed by coordination to metal ion generate exceptionally robust porous solids. Such porous solids retain their internal porosity upon loss of solvates by thermal treatment.

Cyclo-metallated cationic iridium complexes having 2-phenylpyridine (*Hppy*) and 2,2'-bipyridine (*22bpy*) as ancillary ligands are luminescent. In such complexes $\pi - \pi$

stacking interactions involving phenyl rings occur as *face-to-face*, *edge-to-face* and offset *face-to-face*. Due to the repulsions between the two parallel stacked phenyl rings the *face-to-face* stacking is less encountered. Introduction of the intra-molecular $\pi - \pi$ stacking interactions cause distortion of the configuration of *22bpy* ancillary ligands, as a result, such complexes are less photo-luminescent. For example, different fluorinated aromatic as a substituent of ligands in cationic iridium complexes control π -stacking. The complexes [Ir(*ppy*)₂(*F2phzpy*)]PF₆ and [Ir(*ppy*)₂(*F5phzpy*)]PF₆ where *Hppy* is 2-phenylpyridine, *F2phzpy* is 2-(1-(3,5-difluorophenyl)-1H-pyrazol-3-yl)pyridine, *F5phzpy* is 2-(1-pentafluorophenyl-1H-pyrazol-3-yl)pyridine, show blue-green emission with different efficiencies.¹⁰⁶ From the $\pi - \pi$ distance between the centroids of the parallel aromatic rings, it is ascertained that there exists intra-molecular *face-to-face* $\pi - \pi$ interactions as illustrated in Figure 12. It shows that these π -interactions significantly enhance the photoluminescence efficiency of the respective complex in solution. The π -interaction is absent in the complex lacking fluorine atoms on the phenyl group, and it shows a large difference in photoluminescence property from the other complexes having π -interaction.

It is apparent that the chelate complexes, as well as complexes with macrocyclic ligands, can be suitably organized

Figure 11. Self-assembly of metal porphyrin complexes by hydrogen bonds with guest molecule generating robust architecture.

Figure 12. Fluorine containing aromatic units influencing intramolecular $\pi - \pi$ interactions.

through weak π -interactions as well as ordinary stacking among the planar part of the ligands to form organized non-covalently linked assemblies. The metal complexes containing ligand connected through covalent or non-covalent interactions to robust π -donating units such as C_{60} can be incorporated into channels to generate novel properties and modulate catalytic activities.

2.2 Assemblies of nucleobases in inorganic complexes

The self-assembling of nucleobases attract attention due to the fact that self-assembling of natural DNA the replica for gene transcription occurs as a result of base stacking interactions, hydrogen bonds between bases and surrounding water molecules and in many cases through complexation.^{107,108} There are a large number of examples of self-assemblies of metal complexes in which the nucleobases are covalently linked to a component of the ligand that coordinates to the metal ion and the nucleobases part self-assembles to form non-covalent assemblies. There are also nucleobases which coordinate to metal ions and make new templates for self-assemblies. These aspects have been analysed in detail in a review article.¹⁰⁷ On the other hand, the formation of guanine-quadruplex (GQ), a non-canonical nucleic acid structure, requires monovalent metal ions.¹⁰⁹ Guanine-quadruplex comprises of hydrogen-bonded self-assemblies involving four guanines to adopt a square planar tetrad. To form such tetrads **23**, guanine molecules act as hydrogen bond donors as well as acceptors (Figure 13). Multiple number of G-tetrads generally stack to form the guanine-quadruplex assisted by alkali metal ions such as potassium or sodium. Different conformations, and also depending on a number of nucleic acid molecules, they adopt varieties of topologies. Self-association in solution and at the interface of solid and liquid of ferrocene-tethered guanosine derivatives are used to prepare G-ribbons and lamellar G-dimers. In these cases, physisorption affects the formation of the supramolecular assemblies and for such assembling processes metal ions are not necessarily required.¹¹⁰ Since the above-mentioned assemblies are systematically analyzed in review articles,^{107,111} the discussion here is limited to specific aspects of self-assemblies of metal complexes that control the self-assemblies of free nucleobases within their non-covalent assemblies. Such assemblies generate impetus to modulate and stabilize sub-assemblies of different sizes and shape or guide the assemblies of nucleobases within the assembly in a designed manner. The discrete units of protonated and unprotonated as well as hydrated or self-assembled units of nucleobases get encapsulated in various self-assemblies of inorganic complexes. Metal oxalates are widely studied as supramolecular building blocks that are known to stabilise unusual self-assemblies of protonated nucleobases.^{112,113} Theoretical calculations on different types of hydrogen-bonded synthons **25–28** between adeninium cations with

Figure 13. Interaction of potassium ion with four non-covalently linked Guanines found in G-quartet.

copper-oxalate dianion have revealed that there are differences in energy up to a magnitude of 12 kcal/mol (Figure 14a) among the different experimentally observed synthons. Such an energy difference is comparable to the solute-solvent interactions, and hence are tunable by controlling the preparation methodologies from the same substrate combinations. In practice, the copper oxalate complexes having adeninium cations is comprised of a chain of dications held each other by hydrogen bonds. Such chain-like structures are located in between the layers of copper-oxalate complex anions. In these self-assemblies, synthons connecting the anions and cations are not the lowest energy synthon **25** involving carboxylate oxygen atoms of two carboxylates. The observed synthons are formed by the two oxygen of one carboxylate group **26** as illustrated in Figure 14c. This is a clear evidence of synthon competition and it is a common feature in multi-component cocrystals. In this particular example, the self-assembly **31** has the 1H, 9H-adeninium cation (**29**). Density functional theory calculation shows that 1H, 9H-adeninium cation (**29**) is the most stable form followed by 3H, 7H-adeninium cation (**30**) by an energy difference of 0.46 kcal/mol.¹¹⁴

Changing the anionic part of complex influences supramolecular features and self-assemblies of adeninium cation.¹¹⁵ The position of protonation of adenine can be modulated at different acceptor sites in self-assembled structures. For example, ribbon-like structures (**33**) comprising of pairs of differently protonated adeninium cations positioned next to each other. The adeninium cation protonated to have hydrogen atoms at 1- and 9-positions of adenine (**29**) forms hydrogen bonds with another adeninium cation having hydrogen atoms at 3- and 7-positions of adenine (**30**). These hydrogen bonded pairs of cations are held to copper(II) or manganese(II) bis-2,6-pyridinedicarboxylate complex **32** (Figure 15a) through bifurcated hydrogen bonds. This example is a clear indication how the synthon variations

Figure 14. (a) Some possible hydrogen bonded synthons of copper(II) *bis*-oxalate with adeninium cation; (b) two different types of adeninium cations; (c) experimentally observed self-assembly of the 1H, 9H-adeninium cations held by *aqua*-copper(II) *bis*-oxalate anions.

Figure 15. (a) Manganese(II) or cobalt(II) *bis*-2,6-pyridinedicarboxylate complex having two adeninium cations that are protonated at dissimilar positions. (b) Ribbon-like hydrogen bonded structure formed by adeninium cations.

take place by changing anions of the anionic complex to stabilize assemblies of adeninium cations that are protonated at dissimilar positions.

Divalent metal-oxalate complexes with cytosinium cations ($Hcyt)_2[M(ox)_2(H_2O)_2]$ [where *cyt* = cytosine; M = divalent Mn, Co, Cu or Zn ion] exhibits ribbon-like 1D hydrogen bonded cytosinium cations held within anionic

layers formed by metal oxalate anions. The self-assemblies of cytosinium cations are formed by a hydrogen bond between C=O and amine group of adjacent cytosinium cations.¹¹⁶ Cytosinium *aqua*-manganese(II) *bis*-pyridinedicarboxylate complex $[H_2cyt]_2[Mn(pdc)_2(H_2O)] \cdot (cyt)_2 \cdot 6H_2O$ (where *pdc* = 2,6-pyridinedicarboxylate) is an exceptional example of host-guest complex having cytosinium cation and neutral

Figure 16. (a) Host-guest complex of cytosinium aqua-manganese(II) bis-pyridinedicarboxylate with cytosine. (b) Tetrameric cytosine-cytosinium ribbons in the complex.

Figure 17. (a) Cytosinium zinc(II) 2,6-pyridinedicarboxylate dihydrate. (b) Zinc(II) bis-2,6-pyridinedicarboxylate dianions flanking water-assisted assembly of cytosinium cations.

cytosine molecule.¹¹⁷ Each cytosinium cation has hydrogen atoms at 1- and 3-positions. The manganese complex **34** has a pentagonal bipyramidal seven coordinated geometry having two *pdc* ligands and a water molecule attached to manganese(II) ion (Figure 16a). Cytosine molecules form hydrogen bonds to cytosinium cations to form hydrogen-bonded dimers, and four units of *Cyt.Hcyt*⁺ such adjacent dimers are held together by hydrogen bonds forming tetrameric ribbons **35**. These ribbons of length 33.45 Å are formed by hydrogen bonds between neutral and protonated cytosine entities next to each other (Figure 16b). The manganese complex thus provides a means for guest accommodation through interactions of cations of the guest with neutral guests. A similar complex having neutral and protonated cytosine is *(Hcyt)[Ni(nta)(H₂O)₂](cyt)·2H₂O* (where *nta* = nitrilotriacetate).¹¹⁸ In this example, dimers reunite by hydrogen bonds, and form an infinite tape-like molecular sheet that passes through the layer-like assembly of *[Ni(nta)(H₂O)₂][−]* anions. These two examples show the possibilities of having self-assemblies of neutral cytosine

molecules and protonated cytosine cations as infinite chains or as structures of definite dimension within layers of complex anions.

Water also assists in stabilizing hydrogen-bonded cyclic assemblies of cytosinium cations in metal complexes. For example, cytosinium zinc(II) bis-2,6-pyridinedicarboxylate dihydrate has two cytosinium cations stacked parallel to the aromatic ring of pyridinedicarboxylate ligands (Figure 17a). The self-assembly of the cationic part has hydrogen-bonded cyclic sub-assemblies, each sub-assembly comprising of two water molecules bridging two cytosinium cations (Figure 17b) through C=O...H and N-H...O hydrogen bonds. These cyclic sub-assemblies are connected to two cytosinium cations which are hydrogen bonded to Zn(II)-*pdc* anion. Sub-assembly may be considered as an extension of non-covalent synthons expanding domain to provide new replicas within a self-assembly. These aquated domain expanded cationic sub-assemblies are flanked by zinc(II) 2,6-pyridinedicarboxylate anions.¹¹⁹ These examples clearly suggest that the type and oxidation state of metal ions, as

Figure 18. (a) and (b) are two ways to have stack between metal 2,6-pyridinedicarboxylates with or without an intervening aromatic unit; (c) and (d) are two representative examples.

well as the type of ligands on the metal ions, controls the self-assembling properties of nucleobases. Thus, metal complexes have a bigger role to provide the directional architectures with site-specific protonation, hence the above examples may be a useful guide to study the properties of such assemblies, requiring further attention.

2.3 Stacking interactions in host–guest complexes

Chelate-chelate interactions associated with many metal complexes contribute to self-assembling.¹²⁰ There exists ample scope to modulate stacking arrangements in metal chelates through different stimulants such as solvents, counter ions, guests and reaction conditions. These aspects are reflected in self-assembling of metal-*pdc* complexes. π -Stacking interactions among the chelating ligands are prominent in self-assemblies of metal 2,6-pyridinedicarboxylate complexes. They adopt chain-like structures as illustrated in Figure 18a, where the aromatic parts of two independent

pdc ligands from neighboring anions are positioned parallel over each other with or without a planar spacer molecule. Such structures are found in zinc(II) 2,6-pyridinedicarboxylate complexes with different pyridinium cations. For example, the complex $[\text{H}_2\text{tmbpy}][\text{Zn}(\text{pdc})_2] \cdot 5\text{H}_2\text{O}$ has packing pattern like in **38**; whereas the complex $[\text{H}_244\text{bpy}][\text{Zn}(\text{pdc})_2] \cdot 6\text{H}_2\text{O}$ has packing similar to **39** of Figure 18a (Where, *tmbpy* = trimethylenepyridine 44bpy = 4, 4'-bipyridine).¹²¹ The π -separation between the pyridine rings of $[\text{Zn}(\text{pdc})_2]^{2-}$ in complex $[\text{H}_2\text{bpy}][\text{Zn}(\text{pdc})_2] \cdot 6\text{H}_2\text{O}$ is $\sim 4.2 \text{ \AA}$ which is $\sim 3.5 \text{ \AA}$ in $[\text{H}_2\text{tmbpy}][\text{Zn}(\text{pdc})_2] \cdot 5\text{H}_2\text{O}$ (Figure 18c and d). Both these complexes on heating transform to zinc oxide, but decomposition temperatures are different; namely, $[\text{H}_2\text{tmbpy}][\text{Zn}(\text{pdc})_2] \cdot 5\text{H}_2\text{O}$ decomposes at 425°C whereas $[\text{H}_2\text{bpy}][\text{Zn}(\text{pdc})_2] \cdot 6\text{H}_2\text{O}$, at 380°C . The higher thermal stability of the complex $[\text{H}_2\text{tmbpy}][\text{Zn}(\text{pdc})_2] \cdot 5\text{H}_2\text{O}$ is attributed to strong π -stacking interactions in this complex.

Host–guest complexes of these two complexes with 2,7-dihydroxynaphthalene (2,7*dhn*) have striking differences

Figure 19. Interactions between cations, anions, and guest molecules. (a) $[H_2tmbpy][Zn(pdc)_2] \cdot 4(2, 7dhn) \cdot 3H_2O$ (in one of the 2,7-naphthslenediol ring hydrogen atoms were not located in X-ray structure); (b) $[H_244bpy][Zn(pdc)_2] \cdot 2(2, 7dhn) \cdot 5H_2O$.

Host-guest interactions

Exchange of proton of bipyridinium cations to form template

Next guest inclusion

G = Guest; 44bpy = 4,4'-bipyridine

Scheme 1. Different host–guest equilibriums to enhance guest encapsulation.

between them. Though structures of the two complexes are based on identical anions, the difference in the cations causes a different amount of uptake of guest molecules. The amounts of guest dihydroxynaphthalene with respect to per metal ion are 1:2 in complex **41** and 1:4 in complex **42** (Figure 19). Weak C–H... π interaction is involved in the complex having H_2tmbpy cations whereas the other complex is guided by π – π interactions between the guest molecules and cations. In the host–guest complex $[H_244bpy][Zn(pdc)_2] \cdot 2(2, 7dhn) \cdot 5H_2O$ dihydroxynaphthalene rings are stacked over each other and have π -interactions among them. The centroid-to-centroid distance between the ring of naphthalenediol and the ring of a 4, 4'-bipyridinium cation is 3.54 Å. Both the host–guest complexes form to zinc oxide upon heating; the complex **41** forms zinc oxide at 400° and whereas the complex **42** decomposes to zinc oxide at 460 °C. This result also shows that complex having higher thermal stability has π -stacks whereas the other does not but has weak C–H... π interactions.

A recent study¹²² has revealed that the extent of protonation of the organocation derived from bipyridine controls the uptake of phenolic guest molecules in cobalt(II) 2,6-pyridinedicarboxylate complex. 4,4'-Bipyridinium cobalt(II) 2,6-pyridinedicarboxylate hexahydrate forms host–guest complexes with 2,3- or 2,7-dihydroxynaphthalene (guests are abbreviated as 23dhn and 27dhn, respectively, and 44bpy is 4,4'-bipyridine). The compositions of host–guest complexes are different. This difference is explained by the protonation equilibrium guiding guest inclusion process through various template formations as shown in Scheme 1.

In this Scheme, three sets of equilibriums are suggested in which the inclusion of the first guest is just through the host and guest interactions. Whereas, second equilibrium is a reorganization of the host through a protonation-deprotonation scheme of the cation involving accommodation of another guest. In the third step, the modified host–guest complex formed in the second step takes up another guest molecule. From isothermal calorimetry, the binding

Figure 20. 4,4'-Bipyridinium lanthanum tris-2,6-pyridinedicarboxylate.

constants for these three steps in the inclusion of *23dhn* guest, $K_1 > K_2 \approx K_3$ whereas for a similar process with *27dhn*, $K_1 \approx K_3 > K_2$. Accordingly, in the case of *27dhn* a host-guest complex $(\text{H}_244\text{bpy})[\text{Co}(\text{pdc})_2] \cdot 3(27\text{dhn}) \cdot 6(\text{H}_2\text{O})$ was observed. Whereas in the case of *27dnh* as a guest, the driving force of the reaction was towards the third step, hence host-guest complex of $[(\text{H}44\text{bpy})(\text{H}_244\text{bpy})_{0.5}[\text{Co}(\text{pdc})_2] \cdot 3(23\text{dhn}) \cdot 3(\text{H}_2\text{O})]_2$ was observed.

Lanthanum tris-2,6-pyridinedicarboxylate complex **43** (Figure 20) acts as a host for positional isomers 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene. The corresponding host-guest complexes are $(\text{H}_244\text{bpy})_3[\text{La}(\text{pdc})_3]_2 \cdot 3(23\text{dhn}) \cdot 19\text{H}_2\text{O}$, $(\text{H}_244\text{bpy})_{1.5}[\text{La}(\text{pdc})_3]_2 \cdot 3(27\text{dhn}) \cdot 10\text{H}_2\text{O}$.¹²³ Analysis of structures have shown that the interactions between the anions interacting with cations to hold 2,3- or 2,7-naphthalenediols in **44** and **45** have close similarity. In such host templates, two lanthanum tris-*pdc* anions are bridged by hydrogen bonding with one

4,4'-bipyridinium cation. These templates hold the naphthalenediol guest molecules, and the weak interaction schemes in each case are different (Figure 21). These results indicate that changing the anionic template from *bis-pdc* to *tris-pdc* and changing the central metal ion from cobalt to lanthanum, the intake of guest molecule changes, but the nature of guest has an influence to decide the uptake of a number of guest per host molecule.

2.4 Coordination effect of ligand and effect of substituent on ligands in self-assembling

There are a large number of ways in which a 2,6-pyridinedicarboxylate can bind to metal ions as shown in Figure 22. These modes provide versatility to prepare different templates in respective self-assemblies^{124–127} for binding to guest molecules. Major portions of this class of metal complexes have binding mode I (Figure 22), on the other hand, the coordination modes VI–VII are observed only under constraint conditions.

Ethylenediammonium nickel(II) complex, $[\text{H}_2\text{en}][\text{Ni}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}$ (*en* = ethylenediamine) is a conventional 2,6-pyridinedicarboxylate complex.¹²⁸ It forms layer-like structure with interlayer separation 8.2 Å (Figure 23a). Whereas, similar copper complex is a mixed cationic complex having ethylenediammonium dication and also having chelating neutral ethylenediamine with a composition $[\text{H}_2\text{en}][\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2] \cdot [\text{Cu}(\text{pdc})_2]_2 \cdot \text{H}_2\text{O}$. Interesting aspect of the complexes is the layer-like structure of copper(II) bis-2,6-pyridinedicarboxylate anions encapsulates the *bis*-ethylenediamine copper(II) complex cations. Each complex cation is surrounded by for anions and two water molecules which form hydrogen bonds to the anionic part

Figure 21. (a) 2,3-Dihydroxynaphthalene; (b) 2,7-dihydroxynaphthalene in respective host-guest complex with 4,4'-bipyridinium lanthanum tris-2,6-pyridinedicarboxylate.

Figure 22. Different ligation of 2,6-pyridinedicarboxylates.

Figure 23. (a) Layer-like packing in $[\text{H}_2\text{en}][\text{Ni}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}$; (b) Packing pattern of $[\text{H}_2\text{en}][\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2] \cdot [\text{Cu}(\text{pdc})_2]_2 \cdot \text{H}_2\text{O}$.

and completes the cyclic motif for encapsulation. The encapsulated units are hydrogen bonded to free ethylenediammonium dications illustrated in Figure 23b. The copper complex has channels comprising of anions and water molecules where cations are held (Figure 23b). The distance between copper atoms of two adjacent anions is $\sim 9.44 \text{ \AA}$. This larger distance between the layers is due to the presence of the relatively large inorganic cation $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$.

2.5 Solvents and substituents influencing self-assemblies

Water clusters present in fluorescent complexes show much different emission features from their unsolvated complexes. For example, solid state luminescent properties of complexes $\{[\text{Zn}(\text{phen})(\text{dca})_2] \cdot 3\text{H}_2\text{O} \cdot \text{EtOH}\}_n$ and $\{[\text{Zn}(22\text{bpy})(\text{aba})_2] \cdot 4\text{H}_2\text{O}\}_n$ ($\text{phen} = 1,10\text{-phenanthroline}$, $\text{dca} = 4\text{-dimethylam}$

inocinnamate, $22\text{bpy} = 2, 2'\text{-bipyridine}$, $\text{aba} = 4\text{-dimethylaminobenzoate}$), each has different water clusters in their respective self-assembly. They show red shifts in the respective emission spectra with respect to the emission spectra of the corresponding unsolvated complex.^{25,129} Reversible loss of solvent of crystallisation and solvation were observed in these complexes.

Nickel(II) *bis*-2,6-pyridinedicarboxylate possessing monoprotonated 4-aminobenzyl ammonium cation, stabilizes hexameric water clusters. The water clusters are held in channel-like structures (Figure 24a).¹³⁰ On the other hand, $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2][\text{Zn}(\text{pdc})_2] \cdot 7\text{H}_2\text{O}$ possesses centrosymmetric cyclic decameric water clusters (Figure 24b). Such cyclic decamer propagates as infinite two-dimensional chain. Discrete decameric water units are commonly observed¹⁶ but the aggregation of decameric water clusters forming infinite 2D decameric cluster is unusual.

Wide variations in self-assemblies are brought about by varying the amount of coordinated water and charge on the cationic part of a supramolecular anionic templates.^{131,132}

Figure 24. (a) Anions embedding a hexameric water cluster (space filled mode) in nickel-2,6-pyridinedicarboxylate complex possessing 4-aminobenzyl ammonium cation. (b) A decameric water cluster embedded by the anions of the $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2][\text{Zn}(\text{pdc})_2] \cdot 7\text{H}_2\text{O}$ complex (cations are omitted).

Figure 25. Layer-like structures found in (a) $[\text{Na}(\text{H}_2\text{O})_2][\text{Cu}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}$ and (b) $[\text{K}_2(\text{H}_2\text{O})_7][\text{Cu}(\text{pdc})_2]$.

Figure 26. (a) Bis-imidazolium/2-methylimidazolium nickel(II) 2,6-pyridinedicarboxylate complexes; (b) Layer-like structures (crystallographic yz-plane) of $[(2\text{-methylimidazolium})_2][\text{Ni}(\text{pdc})_2]$ and $[(\text{imidazolium})_2][\text{Ni}(\text{pdc})_2]$.

Compositions of copper 2,6-pyridinedicarboxylate complexes possessing sodium, potassium, magnesium, calcium ions are different; respective compositions are $\{[\text{Na}(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}\}_n$, $\{[\text{K}_2(\text{H}_2\text{O})_7][\text{Cu}(\text{pdc})_2]\}_n$ and $\{\text{Ca}(\text{H}_2\text{O})_4[\text{Cu}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}\}_n$, $[\text{Mg}(\text{H}_2\text{O})_5][\text{Cu}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}$. In these complexes copper-pdc anions act as ligand/s to alkali or alkaline earth metal ion. Such complexes undergo cation exchanges easily. A few such complexes show semiconductor-like properties.¹³² Striking difference in sodium and potassium complex arises from aquation and coordination of water molecules. Self-assembly of $\{[\text{Na}(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{pdc})_2] \cdot 2\text{H}_2\text{O}\}_n$ has di-aqua bridged sodium ions forming chain-like structures. Each sodium ion is associated to four-bridging aqua-ligands and two carboxylate oxygen atoms of $[\text{Cu}(\text{pdc})_2]^{2-}$. On the other hand, potassium ions also form non-covalent polymeric networks of $[\text{K}_2(\text{H}_2\text{O})_7][\text{Cu}(\text{pdc})_2]$, where the K^+ ions are linked through three bridged aqua ligands and two terminal aqua ligands to make a *hepta*-coordinated geometry. These differences arise from the difference in size of the cations which changes the angle of alkali metal ions M-O-M bridges. Stacking among the rings of pdc is observed with a distance 3.58 Å between parallel rings (Figure 25). Due to strong electrostatic interactions between alkali metal ions and anions, the interlayer separations in the two complexes are similar.

Solvent-guided self-assemblies of platinum(II) phenylbipyridine-*bis*(phenylisoxazolyl) phenylacetylide adopts a helical structure in toluene and it shows aggregation-induced enhancement of emission and aggregation-induced circularly polarized luminescence, whereas such optical properties are not observed in the solution of the complex in chloroform where it forms non-helical self-assembly.¹³³

Figure 27. A phosphine ligand connected to guadinium (50) and an intermediate formed by self-assembly activating substrate (51).

The substituent on the cation makes a large difference in packing patterns of inorganic assemblies. One such example is *bis*-imidazolium/2-methylimidazolium nickel-pdc complexes.¹³⁴ The packing patterns of two complexes are different, as shown in Figure 26b. Due to the difference the complex with the methyl substituent the packing pattern of the complex 49 adopts layer-like structure with repeat layers composed of two layers hydrogen bonded to each other layers whereas substitute case the repeat layers are monolayers each layer is connected to next layer by hydrogen bonds of intervening water molecules.

2.6 Supramolecular inorganic assemblies in catalysis

There are large numbers of examples where the catalytic effects of metal complexes are tuned by supramolecular interactions at remote sites from the coordination sphere and a few

Figure 28. Supramolecular complexes with interesting reactivity.

of these complexes are designed as enzyme mimics.¹³⁵ There are examples of organometallic catalyst where supramolecular features of the ligands help to increase the rate of a reaction and in selective product formation. Catalytic activity of the $[\text{Rh}(\text{CO})_2(\text{acac})]$ (where *acac* = acetylacetonate) catalyst enhances in presence of phosphine ligands tethered to guanidinium functionality.¹³⁶ The ligand shown in Figure 27 forms complex with rhodium through phosphorus and the guanidinium part forms hydrogen bonds with the carbonyl group of aldehyde. Such intermediate species facilitate the hydrogenation reaction of the carbonyl group.

Self-assembly through complementary hydrogen bonds between pyridone and pyridineamide units attached to chiral cobalt(II)-*salen* complex **52** (Figure 28) is a good catalyst for nitro-aldol condensation reactions.¹³⁷ The self-assembly of monomer of similar cobalt(II)-*salen* complex, though a catalyst, the enantio-selectivity observed in hydrogen bonded dimeric catalyst is upto 97%. The reaction follows second order kinetics in catalyst concentration.

Cobalt(II) complex of aminotrisphenolate ligands **53** possessing two different hemispheres of ligand and cation environment has been reported.¹³⁸ In this complex, one hemisphere formed by cations and other by the complex anion are held together by hydrogen bonds, which are of interest as the metal cation gets embedded in capsule-like structure. This complex is easily oxidised to corresponding cobalt(III) complex and the hydrogen bonded cationic part gets dislodged. Accordingly, reaction with ligands such as

dimethylaminopyridine and 2,2'-bipyridine, replaces the hydrogen bonded cationic part and cobalt(III) complexes are formed by incorporating the reacting ligands as additional counterpart along with tripodal aminotrisphenolate ligand.

Hydrogen-bonded urea taps incorporated to palladium complex¹³⁹ **54** is an efficient catalyst for olefin polymerisation. In such catalytic reactions, advantages of the supramolecular features of aryl urea are utilised. The aryl urea has N–H protons which are less suitable for hydrogen bond than unsubstituted urea and the aryl-group provides steric as well as hydrophobic effect. These effects contribute to enhanced catalytic activity of the palladium complex over the one lacking the urea part in polymerisation reaction of ethylene.

3. Outlook and conclusions

Above discussions suggest self-assemblies guided by ligands of inorganic complexes and their host–guest complexes provide molecular understanding reflecting on the material properties, and to generate assembled structures of simple inorganic ionic complexes with interesting properties.^{140–142} Study on these assemblies at the interfaces provides interesting optical, magnetic, electrical and transport properties and provides a basis for the epitaxial growth of crystals with modified properties with respect to a parent crystal. The strength of

associations with guests and kinetics of delivery caters to understand transport and delivery of guests. Identification of stable host-assemblies from which guest can be easily removed,^{143–148} search for new templates for molecular recognitions,^{149–153} self-assembling leading to properties such as gelation,¹⁵⁴ will continue to be challenges. Host–guest assemblies with comparable sizes and their recognition of, for example, C₆₀ as guest included in metal-porphyrin^{155,156} for photochemical conversion have future ahead. Furthermore, stimulus-guided changes in assemblies will continue to make impacts in processes like resonance energy transfer and other aggregation induced photoluminescence properties. Thus, this rapidly growing topic on self-assemblies of inorganic complexes requires systematic attention and concerted effort on the design and energetics in order to have control on the synthesis and properties.

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