Chapter X
Summary and Conclusion

The design and synthesis of coordination polymers (CPs) and metal-organic frameworks (MOFs) are of great current interest in the area of materials science, where chemistry plays major role, because of their potential applications in gas sorption and storage, catalysis, photo luminescence, chemical sensing, ion-exchange, drug delivery, optical, magnetic and porous materials. The rational design and synthesis of these versatile materials having unique and appropriate structural features with desired functional abilities largely depend on several factors including the metal/ligand ratio, the nature of organic ligands, the type of metal ions and their coordination preferences, the nature of solvent, reaction temperature, counter ion and pH condition of the reaction medium. It is known that even a slight change in any of the above factors can lead to a significant change in the structural features, dimensionality and topology of the final product even for a fixed composition of the reactants. Template-assisted synthesis has been demonstrated to be one of the very effective strategies employed for the design and synthesis of several functionally useful coordination polymers and MOFs wherein a variety of molecular units with 'template abilities' including solvents, poly oxy-anions, metal complexes and cations are shown to play varying extent of structure-directing and functional tuning of the end-products. Among the positively charged organic templates, the alkyl ammonium cations are seen to be unique both by their cationic nature and also because of their highly directional H-bonding abilities which play major role in deciding the nature of supra-molecular assembly, topology and dimensionality of the frame-work materials. Coordination polymers (CPs) and MOF materials have the fascinating benefits of structural and topological versatilities and functional abilities brought about by the range of possible

combinatorial ensembles dictated by metal/ligand ratio, adaptable coordination preferences and spin state changes. Among the multitudes of coordination polymers and MOFs reported so far metal-carboxylate derived systems are seen to be the major ones both by their number and functional use mainly because of the versatile and adaptable coordination and directional abilities of the carboxylate (R-COO$^-$) moieties. While both di- and poly-carboxylate ligands by themselves can yield a wide variety of CPs and MOFs with diverse structural and functional abilities, the 'pillaring' method employing bi-functional neutral ligands like 4,4'-bipyridyl (bpy) has been shown to be a very effective strategy for developing highly useful and robust MOF systems which can function more efficiently. A survey through all the reported CPs and MOFs so far reveal that the majority of them are developed through this 'linker' and 'pillar' strategy using carboxylate ligands as 'linkers' and diamines as 'pillars'. Because of the cationic form of the metal ions, anionic nature of the carboxylate ligands used and neutral nature of the diamine 'pillars' employed the CPs and MOFs formed are often neutral and non-ionic in nature both on the skeletal frameworks and also on their peripheral positions. While diverse functional abilities of these 'neutral' MOF and CP systems have been successfully harnessed, in certain cases the processing ability of these highly inert solid materials for any practical applications is seen to be extremely poor and often impossible, mainly because of their highly insoluble nature. An easy and very effective way to circumvent this major hurdle and facilitate solvent assisted processability on these inert and rigid molecular framework materials can be by transforming the neutral and rigid skeletal framework into an ionic and solvent compatible framework systems by an appropriate strategy. In the present work we employ 'amine-based template' strategy to transform a class of carboxylate derived neutral and insoluble coordination polymers and MOFs into polymeric materials made up

of anionic skeletal framework, facilitating excellent solvent compatibility including significant solubility even in water.

Di-carboxylate and poly-carboxylate based ligands can be either with rigid or flexible 'spacer' moieties and therefore the resulting MOFs and CPs can be with very robust or flexible scaffolding. While MOF materials with robust frameworks have several advantages the ones with flexible skeletal framework also have been shown to manifest some functional use. It has been amply demonstrated that poly-carboxylates with aromatic core can serve as a very stable and rigid scaffolding. In this class benzene di-carboxylates and poly-carboxylates are the simplest ones. Among the three positional isomers of bdc the 1,4- and 1,3-disubstituted isomers are known to result in largely 2- and 3-dimensional MOFs while the 1,2- isomer is seen to form CPs with mostly one-dimensional feature. The inability of the 1,2- isomer to generate 2- and 3-dimensional systems can be attributed mostly to the proximal positioning of the two carboxylate groups at the 1- and 2- positions because of which those two carboxylates get disposed in sterically and coulombically unfavourable form if the COO$^-$ groups are kept coplanar with the aromatic core. To avoid such repulsive interactions one of the carboxylate units is seen to get disposed in a plane perpendicular to the aromatic core. We have seen that in all the 1,2-isomer derived CPs the disposition of the two carboxylates are in the above form though the two carboxylate units show a wide variety and diverse combinations of coordination modes in their complexes.

We have looked at the spatial disposition of the two anionic carboxylate units in the 1, 2-isomer (phthalate moiety) more closely which reveal the possibility of using a non-coordinating cation which can act merely as a charge compensating unit in which case the carboxylate moieties can take part in coordination in its most comfortable mode (η^1-form) very effectively and can result in coordination polymers with simple but unique structural features. To

effectively translate this strategy and generate new varieties of CPs of phthalate ligand we have made use of a series of alkyl amines (both mono- and di-amines) to function as templating and charge-compensating cations. The synthetic procedure we have used is very simple using mostly water as the reaction medium, making our approach 'green' and efficient. We have made use of a variety of metal ions (Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)) to generate this new class of coordination polymers (36 compounds) in which the metal ions act as functional nodes. We could demonstrate through structural characterization (both single crystal XRD and spectral techniques) that in all the cases the amines are in cationic form (by accepting H^+ from phthalic acid) and acting as charge-balancing moieties to the anionic framework formed through $[M(-COO)_4]^{2-}$ units. While the cations derived from mono-amines act as end-capping units to 1-dimensional anionic framework, the diamine derived dications coulombically hold the 1-D anionic frameworks from both sides resulting in 2-dimensionally extended system. In addition to this, the alkyl ammonium cations are also seen to be functioning as structure-directing units through very effective H-bonding with the anionic framework.

In addition to simple phthalate ligands we have also made use of a poly-carboxylate (1,2,4,5-benzenetetracarboxylate, btec) ligand which can be considered as a molecular system made up of 'two fused phthalate units' as it has on either side of the aromatic core two sets of –COOH groups positioned *ortho* to each other. While the template strategy would work in this case also as in the phthalate system, we further expect that the resulting coordination polymer will be of higher dimensionality (mostly 3-dimensional) compared to that of phthalate system. By adopting the 'green-route' as in the earlier case we could synthesize 20 new CPs/MOFs with anionic skeletal framework derived from 'btec' ligands and structurally characterize them by XRD, spectral, thermal and magnetic studies.

The work presented in the thesis consists of ten chapters. In Chapter I, an overview of the coordination polymers is presented along with the recent developments in the area. This chapter also includes a brief review of the applications of coordination polymers and MOFs in various functional applications including gas storage, anion exchange, catalysis, conductivity, luminescence, chirality, magnetism, spin transition behaviour, NLO etc.

Chapter II contains the details on various synthetic strategies, characterization techniques like elemental analysis and the details on IR, UV-visible, EPR and PL studies besides on powder and single crystal X-ray diffraction, thermal studies and variable temperature magnetic measurements.

Chapter III describes the synthesis and detailed characterisation of 1D and 2D coordination polymers of amine templated Co(II) *bis*-phthalates using various aliphatic mono- and di-amines. We could isolate and spectrally characterize 10 water-soluble coordination polymers which include $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2(H_2O)_2]^{2-}[CH_3\text{-}NH_3^+]_2\}_n$ **1**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **2**, $\{[Co\ (OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **3**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **4** , $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)(H_2O)_2]^{2-}[CH_3\text{-}(CH_2\text{-})_3\text{-}NH_3^+]_2\}_n$ **5**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)(H_2O)_2]^{2-}[CH_3\text{-}(CH_2)_4\text{-}NH_3^+]_2\}_n$ **6**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)(H_2O)_2]^{2-}[CH_3\text{-}(CH_2)_5\text{-}NH_3^+]_2\}_n$ **7**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2]^2[CH_3(CH_2)_5NH_3^+]_2\}_n$ **8**, $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[^+H_3N\text{-}(CH_2)_4\text{-}NH_3^+]\}_n$ **9** and $\{[Co(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[^+H_3N\text{-}(CH_2)_6NH_3^+]\}_n$, **10**. Detailed single crystal X-ray diffraction studies could be carried out on **7**, **8** and **9** to confirm their special structural features. In all the compounds, Co(II) ions are linked to carboxylate groups of phthalate moieties through η^1-mode. The coordination of divalent cobalt ion with two doubly deprotonated phthalate moieties produces anionic cobalt *bis*-phthalate frameworks with $R\text{-}NH_3^+/^+H_3N\text{-}R\text{-}NH_3^+$ counter ions occupying the intercalated space. The additions of other ions do not seem to produce any

change of products and the counter ions cannot be replaced by other ions even when they are of the same charge. Some of the compounds exhibit highly selective adsorption of water molecules over pyridine, methanol, ethanol and ammonia, which indicates their possible potential application as sensors for water molecules. Furthermore, magnetic measurements on complexes **7** and **8** up to 2K indicate that there exist weak antiferromagnetic interactions between the metal centres in these complexes. We also studied the structure reversibility upon dehydration /rehydration and the water sensing ability of the alkyl ammonium templated Co(II) *bis*-phthalates.

In Chapter IV is discussed the details on five novel water soluble alkyl ammonium templated Cu(II)-*bis* phthalate coordination polymers $\{[Cu(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **11**, $\{[Cu(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **12**, $\{[Cu(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}(CH_2)_4\text{-}NH_3^+]_2\}_n$ **13**, $\{[Cu(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}(CH_2)_5\text{-}NH_3^+]_2 \cdot 2H_2O\}_n$ **14** and $\{[Cu(OOC\text{-}C_6H_4\text{-}COO)_2][^+H_3N\text{-}(CH_2)_6\text{-}NH_3^+] \cdot 2H_2O\}_n$ **15**, which are synthesized through simple solution route employing aliphatic amines as templating moieties. They are structurally, spectrally (FTIR, UV-visible and EPR) and thermally characterized. The molecular and crystal structure of **11** and **14** could be determined by single crystal XRD technique. In compounds **11-15**, the phthalate moieties around the Cu(II) are seen to lie in the same plane enabling a square planar geometry with interconnected $[Cu(OOC^-)_4]^{2-}$ units leading to a one-dimensional ribbon like framework. The charge neutrality of these anionic frameworks are achieved through protonated amine moieties intercalated between the anionic chains. In the case of diamine templated systems the protonated diamines act as charge-compensating 'pillars' between the 1D anionic $\{[Cu(OOC\text{-})_4]^{2-}\}_n$ networks forming layered 2D assembly. The low temperature magnetic studies (up to 2K) of **14** reveal interesting anti-ferromagnetic behaviour of the compound.

Chapter V describes the synthesis and structural characterization of five coordination polymers (compounds **16-20**) of amine templated Ni(II) *bis*-phthalates, which include $\{[Ni(OOC-C_6H_4-COO)_2(H_2O)_2]^{2-}[CH_3-NH_3^+]_2\}_n$ **16**, $\{[Ni(OOC-C_6H_4-COO)_2(H_2O)_2]^{2-}[CH_3-CH_2-NH_3^+]_2 \bullet 4H_2O\}_n$ **17**, $\{[Ni(OOC-C_6H_4-COO)_2(H_2O)_2]^{2-}[CH_3-(CH_2)_4-NH_3^+]_2\}_n$ **18**, $\{[Ni(OOC-C_6H_4-COO)_2(H_2O)_2]^{2-}[CH_3-(CH_2)_5-NH_3^+]_2\}_n$ **19** and $\{[Ni(OOC-C_6H_4-COO)_2(H_2O)_2]^{2-}[^+H_3N-(CH_2)_6-NH_3^+] \bullet 2H_2O\}_n$, **20**. Single crystal X-ray diffraction studies of compound **19** could also be carried out. Templated ammonium units are seen to induce the directionality and influence packing feature in the system. In the above compounds, Ni(II) adopts an octahedral geometry in which the apical positions are occupied by water molecules and the equatorial positions by the phthalate moieties resulting in interconnected 14-membered cyclic units forming one-dimensional polymeric anionic chain. The anionic framework is seen to get charge neutralized by protonated amine units intercalated between the 1D anionic chains. Unlike in the case of Co(II) *bis-* phthalate system these Ni(II) based polymers are seen to take only octahedral geometry irrespective of the mono or diamine templates employed. Strong affinity of the Ni(II) systems towards H_2O is unique compared to Co(II) based products. Even though coordinated H_2O molecules get expelled thermally at 120^oC they are seen to reabsorb H_2O rather instantaneously reverting to the original O_h geometry. We were able to evaluate Dq, Racah parameter (B'), nephelauxetic ratio (β) and ν_2/ν_1 ratios from their electronic spectra and assess the metal-ligand covalency in them. We could also look at the low temperature magnetisation properties (up to 2K) for **19**.

In Chapter VI is highlighted the synthetic details of one- and two- dimensional coordination polymers of amine templated Zn(II) *bis*-phthalates (**21-26**) and their structural and spectral characterizations. They are $\{[Zn(OOC-C_6H_4-COO)_2]^{2-}[HO-CH_2-CH_2-NH_3^+]\}_n$ **21**, $\{[Zn(OOC-C_6H_4-COO)_2]^{2-}[CH_3-CH_2-CH_2-NH_3^+]_2\}_n$ **22**, $\{[Zn(OOC-C_6H_4-COO)_2]^{2-}[CH_3-CH_2-CH_2-CH_2-CH_2-NH_3^+]_2\}_n$

23, $\{[Zn(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}(CH_2)_5\text{-}NH_3^+]_2\}_n$ **24**, $\{[Zn(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[^+H_3N\text{-}CH_2\text{-}CH(NH_3^+)\text{-}CH_3]\}_n$ **25** and $\{[Zn(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[^+H_3N\text{-}C_6H_{10}\text{-}NH_3^+]\}_n$, **26** They are structurally characterized by elemental analysis and spectral measurements. Compound **21** was characterized by single crystal X-ray diffraction. As expected the protonated amines are seen in intercalated form between the 1D anionic polymeric helical chains formed through interconnected Zn(II) *bis*-phthalates units to charge-compensate the network. These complexes form multi-dimensional networks directed by H-bonding interactions. We were able to evaluate the band-gap of these 1-D hybrid assemblies (**21-26**) through diffuse reflectance spectra. Besides we were able to look at the PL emission properties of these systems.

Chapter VII describes the synthesis and characterization and some functional properties of amine templated Cd(II) *bis*-phthalate systems which include $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[CH_3\text{-}NH_3^+]_2\}_n$ **27**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[CH_3\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **28**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **29**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **30**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2)]^{2-}[CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **31**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}(CH_2)_4\text{-}NH_3^+]_2\bullet H_2O\}_n$ **32**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]_2\}_n$ **33**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[^+H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]\}_n$ **34**, $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[^+H_3N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_3^+]\}_n$ **35** and $\{[Cd(OOC\text{-}C_6H_4\text{-}COO)_2]^{2-}[^+H_3N\text{-}(CH_2)_6\text{-}NH_3^+]\}_n$ **36**. Compounds **29** and **35** could be characterized through single crystal X-ray diffraction. Even though Cd(II) compounds generally adopt structures involving higher coordination number in all our compounds they form only 'CdO$_4$' tetrahedral type units with structures akin to Zn(II) analogues. The charge compensation of the anionic framework was seen to be done by the alkyl ammonium cations as in other cases. We could develop both 1D and 2D type systems using mono-amines and diamines as templates. Compounds **27-36** are seen to exhibit strong fluorescent emission

properties which indicate their potential use as inorganic-organic photoactive materials.

Chapter VIII describes the design and synthesis of an interesting extension of phthalate systems studied so far as the 1,2,4,5-benzenetetracarboxylate (btec) ligand can be considered as 'two fused phthalate' systems. Both soft solution based and hydrothermal routes have been employed for the synthesis of Cu(II) and Ni(II) based MOFs and CPs derived from 'btec' ligand using template technique. We have successfully synthesized and structurally characterized nine 1-, 2- and 3- dimensional coordination polymers of btec ligand viz., $\{[Cu(C_6H_2COO\}_4)]^{2-}[CH_3-NH_3^+]_2 \cdot 2H_2O\}_n$ **37**, $\{[Cu(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-NH_3^+]_2\}_n$ **38**, $\{[Cu(C_6H_2\{COO\}_4]^{2-}[CH_3-(CH_2)_3-NH_3^+]_2\}_n$ **39**, $\{[Cu(C_6H_2\{COO\}_4)]^{2-}[CH_3-(CH_2)_4-NH_3^+]_2 \cdot 2H_2O\}_n$ **40**, $\{[Cu(C_6H_2\{COO\}_4)]^{2-}[CH_3-(CH_2)_5-NH_3^+]_2 \cdot 4H_2O\}_n$ **41**, $\{[Cu(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_2-NH_3^+] \cdot 2H_2O\}_n$ **42**, $\{[Cu(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_3-NH_3^+] \cdot 4H_2O\}_n$ **43**, $\{[Ni(C_6H_2\{COO\}_4)(H_2O)_4]^{2-}[^+H_3N-(CH_2)_2-NH_3^+] \cdot 3H_2O\}_n$ **44** and $\{[Ni(C_6H_2\{COO\}_4)(H_2O)_4]^{2-}[^+H_3N-(CH_2)_3-NH_3^+] \cdot 2H_2O\}_n$ **45**. Out of these **37**, **38**, **42** and **44** could be characterized by single crystal XRD technique. All the polymers are seen to contain alkyl ammonium cations as templating units. The templated Cu(II)(btec) system **38** is seen to form two-dimensional sheet like structure while **37** forms a 3D frame work. In the diamine derivatives (**42** and **43**) the protonated diamines not only maintain charge neutrality but also coulombically interconnect the anionic frameworks to form an overall 3D structure. However in Ni(II) derivatives (**44** and **45**), a one-dimensional chain of $[Ni(C_6H_2\{COO\}_4)(H_2O)_4]^{2-}$ is formed in which two of the deprotonated *p*-carboxylates remain non-coordinating while the two carboxylates units *para* to each other act as a linker between two metal atoms through strong coordination. We have also investigated the low temperature magnetic studies of compounds **37** and **38**. The magnetic data obtained for **38** is seen to be

interesting while **37** is seen to be essentially a paramagnetic system. This may be due to the 2D structure and the closeness of Cu-Cu distances in compound **38,** while in compound **37** the 3D structure results in larger Cu-Cu distances.

Chapter IX describes 11 MOF materials (**46-56**) derived from 'btec' ligand out of which some of them have porous features. They are synthesized using Co, Zn and Cd metal salts btec and aliphatic amines. All these compounds are characterized by spectral and other analytical techniques. Compounds **46**, **48** and **56** could be structurally characterized through single crystal X-ray diffraction techniques. The characteristic feature of these prepared complexes is their porous nature having 3-dimensional framework arrangement with excess negative charge and channel-like voids, which accommodate H_2O molecules and protonated amine moieties. The compounds synthesized and studied are $\{[Zn(C_6H_2(COO)_4)]^{2-}[CH_3-NH_3^+]_2 \bullet 4H_2O\}_n$ **46,** $\{[Zn(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-NH_3^+]_2 \bullet 2H_2O\}_n$ **47,** $\{[Zn(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-CH_2-CH_2-NH_3^+]_2 \bullet 0.5H_2O\}_n$ **48,** $\{[Zn(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-CH_2-CH_2-CH_2-NH_3^+]_2\}_n$ **49,** $\{[Zn(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-NH_3^+]_2\}_n$ **50,** $\{[Zn(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_2-NH_3^+] \bullet 5H_2O\}_n$ **51,** $\{[Cd(C_6H_2\{COO\}_4)]^{2-}[CH_3-CH_2-CH_2-CH_2-NH_3^+]_2 \bullet 3H_2O\}_n$ **52,** $\{[Cd(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_2-NH_3^+] \bullet 4H_2O\}_n$ **53,** $\{[Cd(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_3-NH_3^+] \bullet 7H_2O\}_n$ **54,** $\{[Cd(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_4-NH_3^+] \bullet 2H_2O\}_n$ **55** and $\{[Co(C_6H_2\{COO\}_4)]^{2-}[^+H_3N-(CH_2)_6-NH_3^+] \bullet H_2O\}_n$ **56,** The structural diversity shown by these amine templated compounds are very interesting. Compounds **46-55** show excellent photoactive properties (emission) due to LMCT and can be expected to behave as useful functional materials for light emitting devices.

To conclude, in this work we have synthesised 56 new 1D chain, 2D sheets or 3D frame work materials through soft solution route by mixing the reagents at moderate temperature conditions followed by slow evaporation at room temperature. We could get high quality single crystals in most of the cases.

Single crystal X-ray diffraction studies and various other spectral, magnetic and thermal studies show that all of the isolated complexes have anionic skeletal frameworks formed by the carboxylate groups of benzene poly carboxylates. The charge compensation of these polymeric chains, sheets or frameworks is achieved by the protonated amines which are seen, in certain cases contributing to the dimensionality of the coordination polymers. A few of the synthesized compounds show interesting functional properties like anti ferromagnetism, photoluminescence, etc. which have been examined in some detail in certain cases. Coordination polymers are mostly insoluble in nature. But the coordination polymers or MOFs we have discussed in the work show significant solubility in water. This is due to the presence of the polymeric anionic skeletal frame works. Further extension of this approach to the synthesis and application of other polymeric networks is in progress, especially from their functional application point of view.