Crystal engineering of coordination polymers using 4,4′-bipyridine as a bond between transition metal atoms

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Coordination polymers have attracted an enormous interest among chemists due to their novel physical and chemical properties. This review describes the role of 4,4′-bipyridine in discovering various coordination polymers with novel topologies that range from one-dimensional to three dimensional. The geometries of coordination polymers of bipy include linear, zigzag, four-fold helices, molecular antenna, ladder, railroad, double, triple and quadruple chains, bilayer, square and rectangular grid, honeycomb layers, Lincoln Logs, 3D frames, diamondoid, $4^2 \cdot 8^2$ and cubic networks.

Introduction

Crystal engineering of coordination polymers is an emerging area of research with several potential applications in areas such as catalysis, conductivity, porosity, chirality, luminescence, magnetism, spin-transition and non-linear optics.[1–3] The riches in the fundamentals of coordination chemistry laid the foundation to the development of this field.[4] On the other hand the emergence of supramolecular chemistry,[5] which largely dealt with discrete self assemblies *via* coordination bonds or hydrogen bonds in solution, and crystal engineering,[6,7] which dealt with designing new materials with predefined properties based on non-covalent interactions, fuelled the development of coordination polymers. Although the term coordination polymer was coined in 1964,[8] the principles of "crystal engineering" for designing coordination polymers were not applied until 1995.[9]

Several recent reviews have projected about the gigantic raise in the number of publications of coordination polymers per year since 1990 onwards.[3b,e,15b] In the majority of coordination polymers, either the O-atoms of anions (carboxylates, nitrates, sulfates, phosphates, phenolates) and/or the N-atoms of cyanates, cyanides, amines, pyridines engage in coordination bonds with transition metal atoms (Tr–O and Tr–N). A Cambridge Structural Database (CSD) search indicates that the coordination polymers propagated by Tr–O (7074 hits) are the major variety compared to those of Tr–N (6392 hits).[10] In about 53% of the Tr–O variety, the O-atom belongs to carboxylates whereas in about 40% of the Tr–N variety the N-atom belongs to pyridine. These statistics indicate the importance of carboxylate and pyridine moieties in generating coordination polymers. Furthermore, the raise in the crystal

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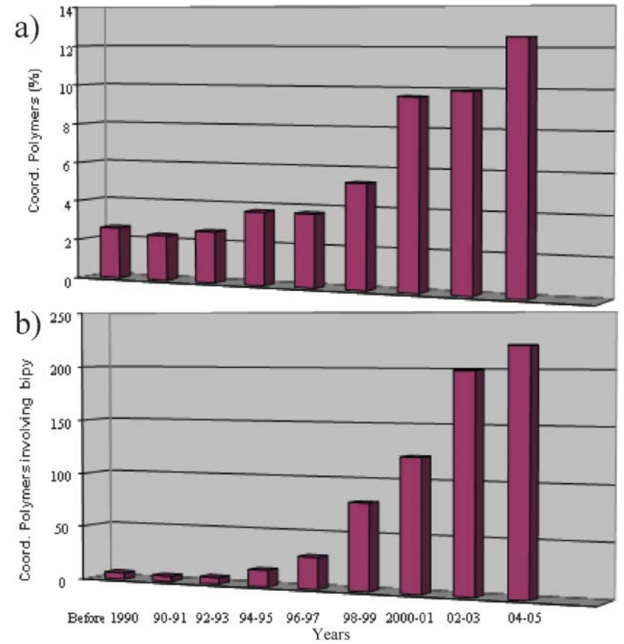


Fig. 1 Histograms (a) percentage of crystal structures of coordination polymers in the crystal structures of metal–organic complexes; (b) number of crystal structures of coordination polymers involving bipy.

structure determinations of coordination polymers in recent years is apparent from Fig. 1a.

The importance of 2,2′-bipyridine as a ligand in coordination chemistry has been reviewed.[11] The present review will focus upon the studies of coordination polymers based on 4,4′-bipyridine (bipy) and transition metals. Currently, the database contains 2467 structural determinations for pyridine based coordination polymers. Remarkably, 683 (30%) of the 2467 structures belong to only one ligand, that is 4,4′-bipyridine. Furthermore, prior to 1990 only five coordination polymers using bipy were published. However, the steep raise in the number of crystal structures of coordination polymers of bipy from 1990 can be seen in Fig. 1b.

The ligand 4,4′-bipyridine is an ideal connector between the transition metal atoms for the propagation of coordination networks due to the following features: it has two potential binding sites which are arranged in a divergent (*exo*) fashion; has a rigid structure which will help in the predictability of the network geometries; the length of the ligand is good enough to create the cavities of molecular dimensions upon the formation of the networks with metal atoms. In principle, the pyridyl groups of bipy can rotate along a central C–C bond. However, the rotation does not affect the mutual orientation of the two lone pairs. Therefore bipy can be regarded as rigid and a prototypical bridging ligand.

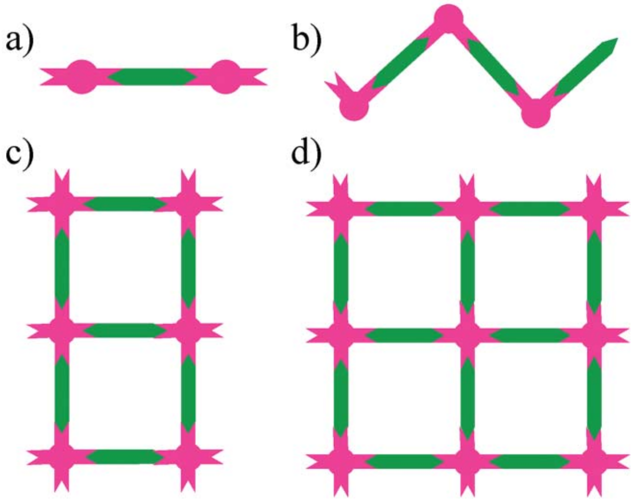
Table 1 Number of coordination polymers of bipy with various transition metal salts[a]

Metal	NO_3^-	XO_4^-	COO^-	SCN^-	X^-
Cu(191)	16	24	70	2	23
Co(112)	30	2	49	4	3
Zn(110)	8	7	52	2	9
Cd(74)	16	3	21	2	17
Ni(69)	16	4	30	2	2
Mn(51)	0	1	23	3	5
Fe(34)	0	4	10	3	1
Ag(29)	5	1	8	0	1

[a] The numbers in the parenthesis indicates total no. of polymeric structures, X is any halide, data are taken from CSD.

Curiously enough, bipy was shown to form a variety of networks ranging from one-dimensional to three-dimensional (Table 1) with several transition metal salts. The geometry of the architectures was shown to depend on several factors such as coordination geometry of the metal atom, the presence of guest molecules, ligand and transition metal ratios and anions (Scheme 1). Inspired by the coordination polymers of bipy several tailored derivatives of bipy were synthesized by inserting various spacers between pyridine moieties. The spacers range from rigid aromatic to flexible aliphatic groups.[3e,12] Most of these modified ligands have been shown to form coordination polymers with transition metals similar to bipy. The majority of these polymers exhibited huge cavities/channels of molecular dimensions and/or various functional properties.

The syntheses of these coordination polymers involve the reaction of bipy with transition metal salts in suitable solvents. The formed product has to be perfectly crystalline for proper characterization. Otherwise one has to find different reaction conditions by changing the solvents, anions, guest molecules, concentrations and ratios of the components. Sometimes it is highly tedious to find out the suitable conditions for the formation of the crystals of a coordination polymer for given components. Part of the reason deals with the insolubility of the coordination polymer formed. Formation of powders can be avoided, to some extent, by selecting metal atoms that form labile coordination bonds. Accordingly, the coordination polymers of bipy are well populated with metal ions such as Cu(I) or Cu(II), Ag(I), Cd(II), Zn(II), Co(II) and Ni(II). In general, three procedures have been adopted for the syntheses of coordination polymers: (a) direct mixing of bipy and metal salt solutions; (b) diffusion of a metal salt solution into a bipy solution by layering them on top of each other; (c)



Scheme 1 The most frequently occurring coordination polymers of bipy and transition metals: (a) linear chain (97); (b) zigzag chain (26); (c) ladder (12); (d) square grid (38). Green connectors represent bipy and pink nodes represent metal atoms.

hydrothermal or solvothermal synthesis in which the components and H_2O or a solvent were heated in a sealed tube to very high temperatures for certain time and allowed to form crystals by slow cooling.

Although several coordination polymers are designed to date and several useful functional properties were discovered, the predictability of the network geometry of coordination polymer is still a challenging problem.[13] The predictability is affected by several factors. Partly it is due to the use of labile metal ions, which are not so selective to their coordination environment and geometry. Use of flexible ligands further hampers the predictability as flexible ligands can exist in more than one conformation. Interpenetration is another problem which has to be addressed properly while designing new structures. Finally it all depends on the process of crystallization, which deals with the optimization of the various possible interactions between metal, ligand, anion, solvent and guest molecules. Therefore while designing coordination polymers, it is important to apply the knowledge of intermolecular interactions that is available from crystal engineering studies of organic molecules. Crystal engineering deals with observation, rationalization and predictability.[14] Hence the review of the good amount of data which is available on coordination polymers of bipy was anticipated to give better inputs for the predictable formation of the coordination networks with bipy and various related ligands.

We present this article with respect to the anions, as it is a well accepted fact that the anions have a major influence on the network geometries.[12] Several anions were used to construct coordination polymers of bipy with transition metals. We have categorized them into three sections based on the complexity of their coordination modes. Nitrate, perchlorate and YF_6 (Y = P, Si, Sb and Ge) anions are grouped together as they are often silent spectators in network propagation and form a limited number of coordination modes. Halide ions and carboxylates are presented separately as both these anions form metal clusters and interfere in the network propagation. Concerning the carboxylates, we have considered bipy coordination polymers containing mono carboxylates, as the number of carboxylates in the structure increases the complexity and decreases the predictability to some extent.[15] Furthermore, bipy was shown to link mixed metal anion clusters to form various networks and also shown to act as pillars between metal–anion layers.[1c] However, due to space constraints we have not included those studies in this review.

The first coordination polymer with bipy

The first coordination polymer of bipy with an X-ray single crystal structure determination was reported in 1982.[16] This polymer is formed by the treatment of bipy with Co(dimethylglyoximate)$_2$. The Co(II) has an octahedral geometry as both the anions coordinate with it in a bidentate fashion. The ligand bipy joins the metal dianion species to form a 1D polymer with a linear geometry (Fig. 2a).

Polymers with 1,3-diketone or xanthate as the anions

Following the above structure, three coordination polymers with bipy were published in 1985–86: two structures with Cu(II) and 1,3-diketone and one structure with Ni(II) and butylxanthate.[17] All three have a linear geometry similar to the above structure but the polymer of bipy with Ni(II) and xanthate was shown to include two CCl_4 molecules per metal atom (Fig. 2b). Furthermore, in the presence of butylxanthate, bipy with Cu(II) has shown the tendency to generate another type of 1D polymer which has a zigzag geometry.[18] Although, in this polymer Cu(II) has the octahedral geometry the coordination environment is different from the above. Interestingly, the zigzag variety with xanthate was also shown to include $CHCl_3$ and EtOH as guest molecules (Fig. 2c). Notably, the number of coordination polymers of bipy with these anions is very low.[19]

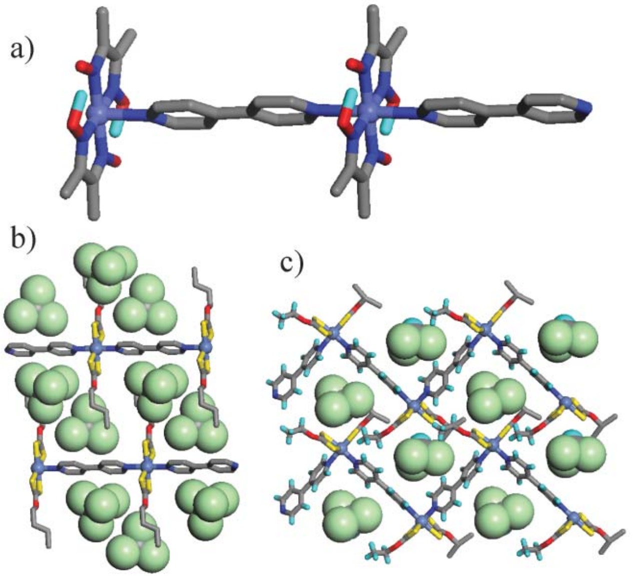


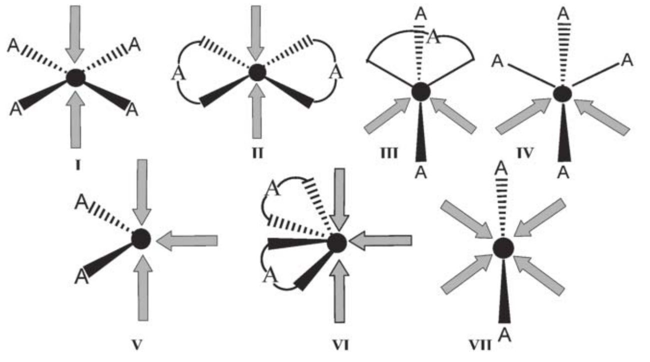
Fig. 2 Illustrations for the coordination polymers: (a) linear chain; (b) entrapment of solvent by linear chains; (c) zigzag chains when the anion is xanthate.

Polymers of bipy when the anions are nitrates or perchlorates, thiocyanates or YF_6 ions

In the presence of these anions bipy with various transition metal atoms was shown to propagate several networks ranging from 1D to 3D. These anions are grouped together as all are inorganic and form predictable coordination modes. Furthermore, these anions were involved much less frequently in the metal cluster formations in the presence of bipy. The coordination modes of transition metal atoms to propagate in 1D, 2D and 3D with these anions is shown in Scheme 2.

One-dimensional polymers

The majority of the polymers of bipy and transition metal atoms belong to the 1D polymers. The primary reason could be due to the competition of anions and other ligands, which include bidentate ligands, excess of bipy, H_2O, MeCN *etc.*, to coordinate with the same transition metal atom. Furthermore, the reaction conditions and solubility of the product formed also influence the geometry and dimensionality of the network. These 1D polymers, based on their geometry, were categorized as linear, zigzag, ladder, molecular antenna and railroad.



Scheme 2 Various coordination geometries in the presence of NO_3, ClO_4 and MF_6 anions. **I–IV** leads to 1D networks, **V–VI** leads to 1D–3D networks, **VII** leads to 2D and 3D networks. Blocked arrows represent the coordination of bipy units. A = anion/monodentate ligand in **I** and **IV**; A = anion or bidentate ligand in **II** & **III**; A = NO_3^- in **V–VII**.

Zigzag and linear polymers. The transition metals with nitrate or perchlorate as anions have shown the tendency to form linear or zigzag coordination polymers with bipy (Fig. 3). In these polymers the metal atom exhibits octahedral geometry but only two coordination sites of transition metal were used to propagate the network. Arrangement of these coordination sites in a *trans* fashion generates a linear polymer, while a *cis* arrangement leads to a zigzag polymer. The other four coordination sites are occupied by H_2O and/or anions in monodentate or bidentate fashion (**I–IV**).[20] The use of ancillary ligands such as ethylene diamine or 2,2′-bipyridine had resulted in zigzag networks as they exhibit coordination geometry **III** (Fig. 3b).[21] Further, the presence of excess bipy in these reactions resulted in the molecular antenna network, in which bipy acts as a monodentate as well as bidentate ligand and also as a guest (Fig. 3c & 3d).[22]

Ladder and railroad networks. In these networks three coordination sites of transition metal are coordinated by bipy in a T-shape arrangement to propagate the ladder.[23] Ladder networks were found to form with Ni(II), Co(II) and Zn(II) metals and most preferably when the anion is nitrate (Fig. 4). To date a total of twelve ladder networks were reported using bipy. These structures differ from each other in coordination geometry of the metal and inclusion of guest molecules. In ladders, Ni(II), Co(II) and Zn(II) were found to exhibit tbp (**V**), pbp (**VI**) and octahedral geometries (**VII**) respectively. The guest molecules included in the ladder networks range from small solvent molecules such as diethylether to big molecules such as pyrene.

Furthermore, only one ladder like structure was reported in the presence of ClO_4 anion.[24] In this structure the metal (Ni(II)) adopts an octahedral coordination and three coordination sites were used for network propagation. The other three coordination sites are occupied by two water molecules and an additional bipy which acts as a monodentate ligand. The geometry of the structure resembles a railroad (Fig. 4b).

Two-dimensional networks

These networks include bilayers, square grids and rectangular grids. All these networks contain huge cavities to include the guest molecules. In the absence of guest molecules self interpenetration of the networks was observed.

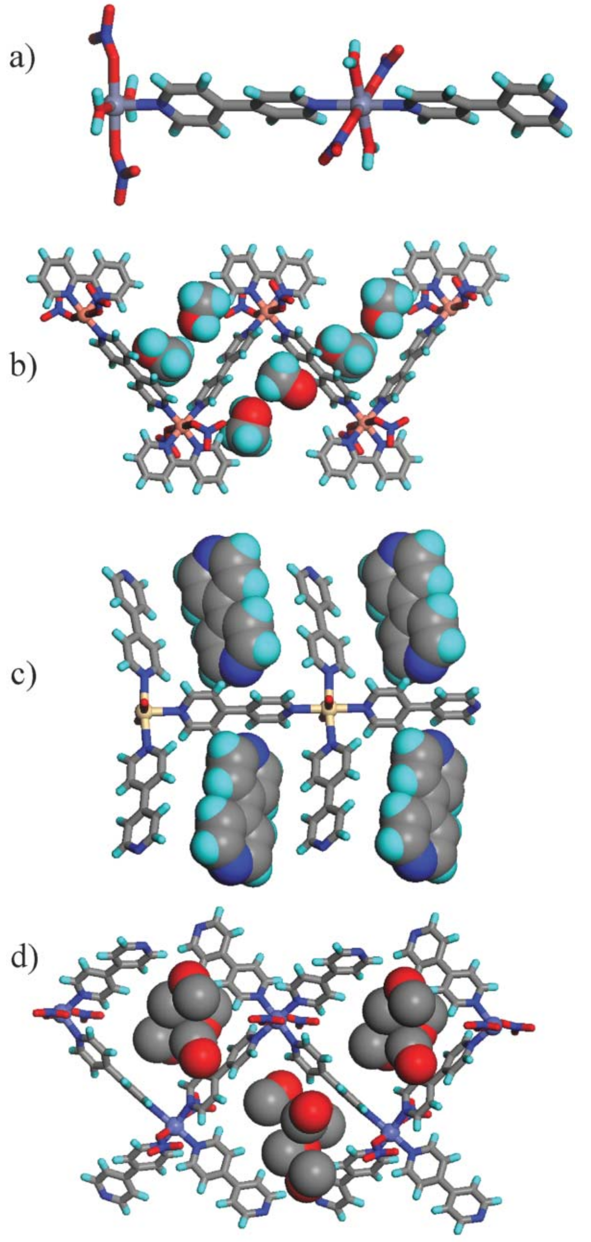


Fig. 3 (a) 1D linear chain; (b) zigzag chain, guest MeOH (space filling mode); (c) molecular antenna, guest bipy (space filling mode); (d) zigzag chains in which two bipy units act as monodentate ligands, guest MeOH are in space filling mode.

Bilayer network. Conventional bilayers of lyotropic liquid crystals contain hydrophobic and hydrophilic layers in an alternate fashion. However in coordination bilayers, the two layers are identical in nature but are separated by a ligand. Both the layers of a bilayer contain a set of one-dimensional chains arranged in a parallel fashion. Furthermore, the chains in one layer make an approximate angle of 90° with those of the other layer and the metal atoms were found to adopt the coordination geometries **V** and **VI**. In fact, the first bilayer structure was observed between the somewhat flexible ligand

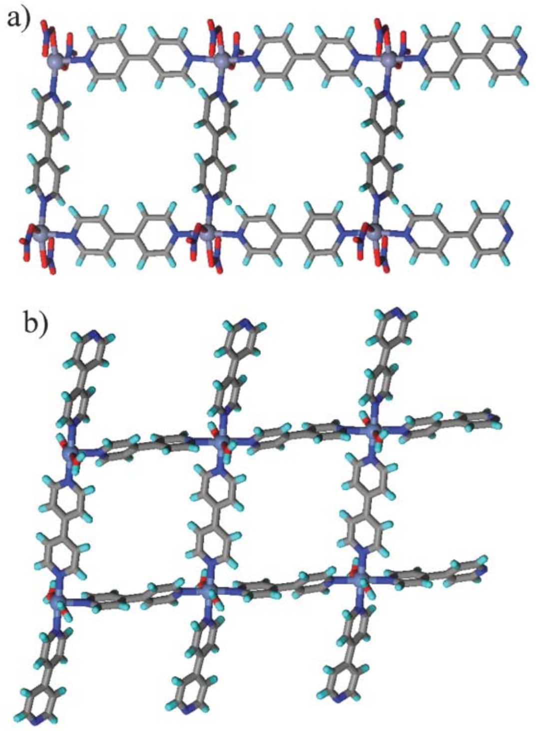


Fig. 4 Representation of (a) molecular ladder and (b) railroad.

1,2-bis(4-pyridyl)ethane and $Co(NO_3)_2$.[25] Subsequently, these bilayer structures (Fig. 5) were also observed for bipy with $Co(NO_3)_2$ (nine structures), $Ni(NO_3)_2$ (two structures), $Cd(NO_3)_2$, $Cu(ClO_4)_2$, and $Cu(PF_6)_2$.[26] The guest molecules included in these networks are H_2O, CS_2, THF, EtOH, CH_3CN, MeOH, DCM and acetone. Bilayer networks were shown to be stable even after removal of the solvent molecules and exhibited gas absorption properties with CH_4, O_2, N_2, CO_2 and N_2 gases.[26d]

Square grid networks. Among all the networks of coordination polymers the 2D networks with (4,4) or square grid geometry are the most prominent variety. In these networks the metal atom adopts octahedral geometry with four ligands at the equatorial positions and two counter anions or water molecules at the axial positions. The most exploited metal atoms for square grid networks (23 structures) with nitrates as anions are Cd(II), Co(II), Ni(II) and Cu(II).

The first square grid coordination polymer using bipy was reported by Robson *et al.* in the crystal structure of $\{[Zn(bipy)_2(H_2O)_2][SiF_6]\}_n$.[27] The cavities in the layer have an approximate square shape with the Zn to Zn separation of 11.44 Å. However, given the big size of the grid cavity, the networks are doubly interpenetrated (Fig. 6a). Due to the interpenetration of the networks the crystal lattice achieved the efficient packing in which the average volume occupied by a non-hydrogen atom is only 14.6 Å^3. Later Kitagawa *et al.* reported similar structures with Cu(II) salts.[26f] Further, this type of interpenetration in bipy square grids was observed only in the presence of SiF_6 anions.

The non-interpenetrated or open square grid polymer with bipy was first observed in the crystal structure of $\{[Cd(bipy)_2(NO_3)_2]\cdot 2(o\text{-dibromobenzene})\}_n$.[28] The guest molecules were included in the cavities by eschewing the interpenetration of the networks (Fig. 6b). The layers in the structure consist of perfectly planar squares with the Cd to Cd separation of 11.8 Å. Each square cavity accommodates two molecules of *o*-dibromobenzene. The layers pack on each other with an interlayer separation of 6.3 Å. Furthermore, the square cavities were found to show shape selective inclusion: only *o*-dihaloaromatic compounds, and not their *meta* and *para* analogues, were included.

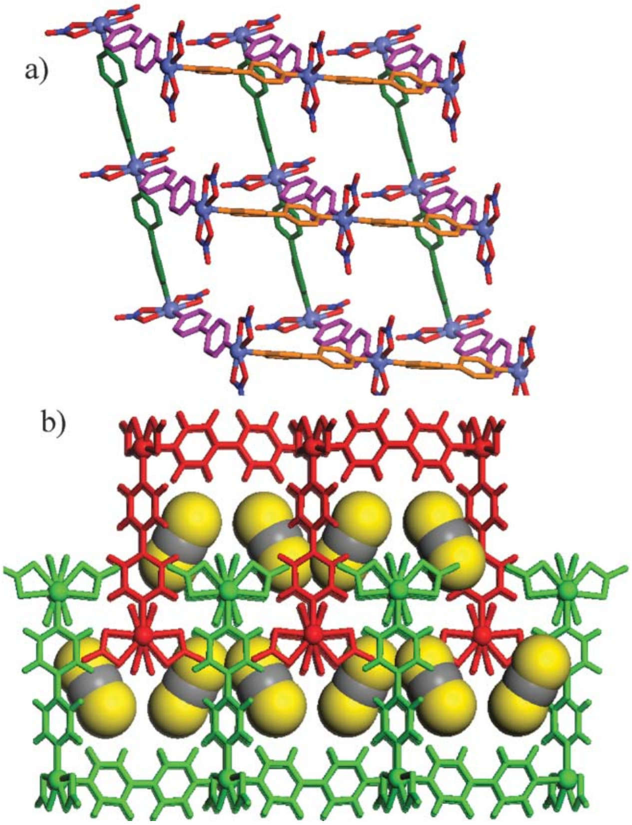


Fig. 5 (a) Bilayer architecture, the top (orange) and bottom (green) layers were joined together by the middle bipy (magenta) units. (b) Interdigitation of bilayers to include the guest molecules (CS_2 in space filling mode).

Square grid networks of bipy with $Ni(NO_3)_2$ or $Co(NO_3)_2$ were studied by Zaworotko *et al.*[29] In these studies the square grid networks were prepared in the presence of several types of guest molecule. For example, hydrocarbons as diverse as benzene and pyrene and also electron rich (napthalene, anisole and veratrole) and poor (nitrobenzene) molecules were included as guests. From these studies it was shown that depending on the host–guest stoichiometry, the interlayer separation can vary from 6 to 8 Å and the square grid networks can pack on each other in three types of packing modes.[1d] In addition, some of these grid structures reveal that the guest molecules can form networks of their own by interacting with each other *via* aromatic interactions. Such non-covalent networks of guest molecules were found to interpenetrate through square grid networks. These structures provide a unique opportunity for the coexistence of covalent

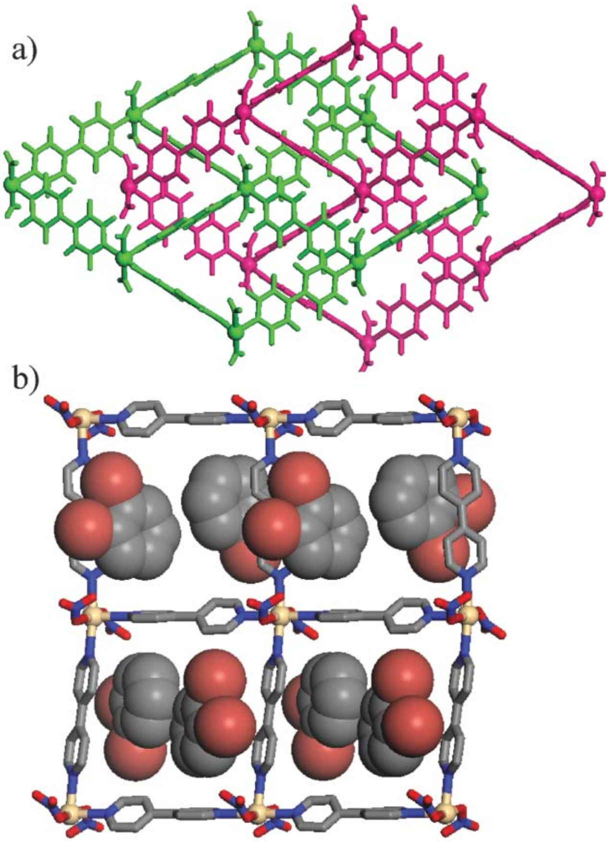


Fig. 6 (a) Doubly interpenetrated square grid networks, H_2O in axial positions; (b) Open square grid network, nitrates in axial positions and the guest molecule is *o*-dibromobenzene (space filling mode).

and non-covalent networks in a crystal lattice. The ligand bipy was also shown to form similar open square grid polymers with $Cd(ClO_4)_2$, $Zn(ClO_4)_2$, $Cu(ClO_4)_2$, $Ni(SCN)_2$ and $Co(SCN)_2$.[30] Even bigger square grid structures with the dimensions of 15 × 15, 20 × 20 and 25 × 25 Å have been reported, using bigger ligands than bipy.[31a–c]

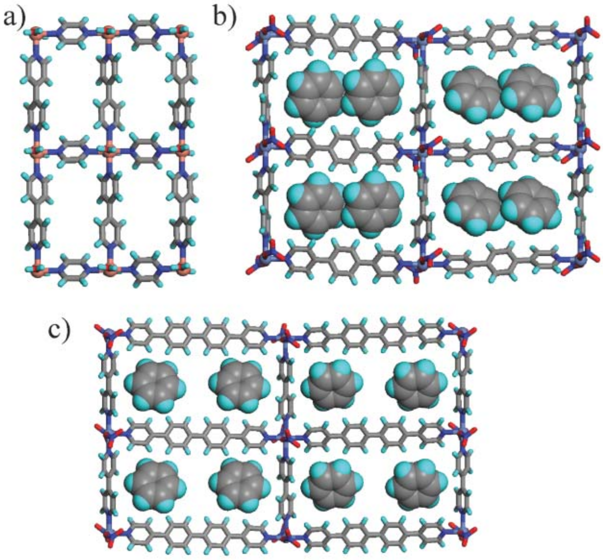


Fig. 7 Rectangular grids of different dimensions: (a) 5 × 10; (b) 10 × 15 and (c) 10 × 20 Å. Benzene molecules (space filling) have been included in the rectangular cavities.

Rectangular grids. The reaction of bipy and other *exo*-bidentate ligands, which are shorter or longer than bipy, with transition metal salts was resulted in the selective formation of rectangular grid networks.[31d,e] The first cationic rectangular grid with dimensions 6.8 × 11.2 Å was prepared by Chen *et al.* by the reaction of bipy and pyrazene with $Cu(PF_6)_2$. The Cu atom adopts an elongated octahedral geometry with two moieties of bipy and two moieties of pyrazene at the equatorial positions and two water molecules at the axial positions (Fig. 7a). The offset superposition of each pair of adjacent layers by half of the longer edges resulted in the smaller rectangular channels (*ca.* 5.6 × 6.8 Å) that are occupied by PF_6^- ions. Subsequently, bigger rectangular grids of dimensions 11.3 × 15.6 and 11.3 × 19.9 Å were prepared by using ligands which are bigger than bipy and pyrazine (Fig. 7b & c). These grids were shown to include benzene molecules. In fact, the benzene molecules themselves form layers, which contain huge cavities, *via* aromatic interactions. The coordination network and the network of benzene molecules interpenetrate with each other *via* edge-to-face aromatic interactions between benzene and the ligands.

Three-dimensional networks

Compared to 1D and 2D networks, the 3D networks which are propagated exclusively by bipy and transition metal atoms are relatively rare. In these networks the metal atoms can act as three connected and four connected nodes.

Networks propagated by 3-connected nodes. There are two possible coordination modes for three connected nets: T-shape and trigonal. Two types of 3D networks are reported with T-shape geometry: one with $Ag(NO_3)$ and the other with $Co(NO_3)_2$. Bipy upon treatment with $Ag(NO_3)$ resulted in a triple interpenetrated 3D network (Lincoln Logs†).[32a,b] The Ag(I) atoms are coordinated linearly by two bipy units to propagate the chains and these chains are connected by Ag···Ag interactions to form a 3D network (Fig. 8a). The reaction of $Co(NO_3)_2$ upon treatment with bipy in the presence of benzene and pyridine lead to the formation a triple interpenetrated 3D network.[32c] Three units of bipy coordinates to Co(II) in a T-shape and the nitrates coordinate to Co(II) in bidentate and monodentate fashion (Fig. 8b). Another 3D network reported with bipy and Cu(I) in which the metal atom adopts trigonal geometry.[32d] The hydrothermal treatment of $Cu(NO_3)$ and bipy in the presence of 1,3,5-triazine was shown to form six-fold interpenetrated 3D networks (Fig. 8c). Recently, similar network was also reported by the reaction of bipy with $Cu(ClO_4)$.[32e]

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† Lincoln Logs are a toy consisting of notched miniature logs, about 1–2 cm in diameter. Analogous to real logs used in a log cabin, Lincoln Logs have notches in their ends so that small model log buildings can be built.

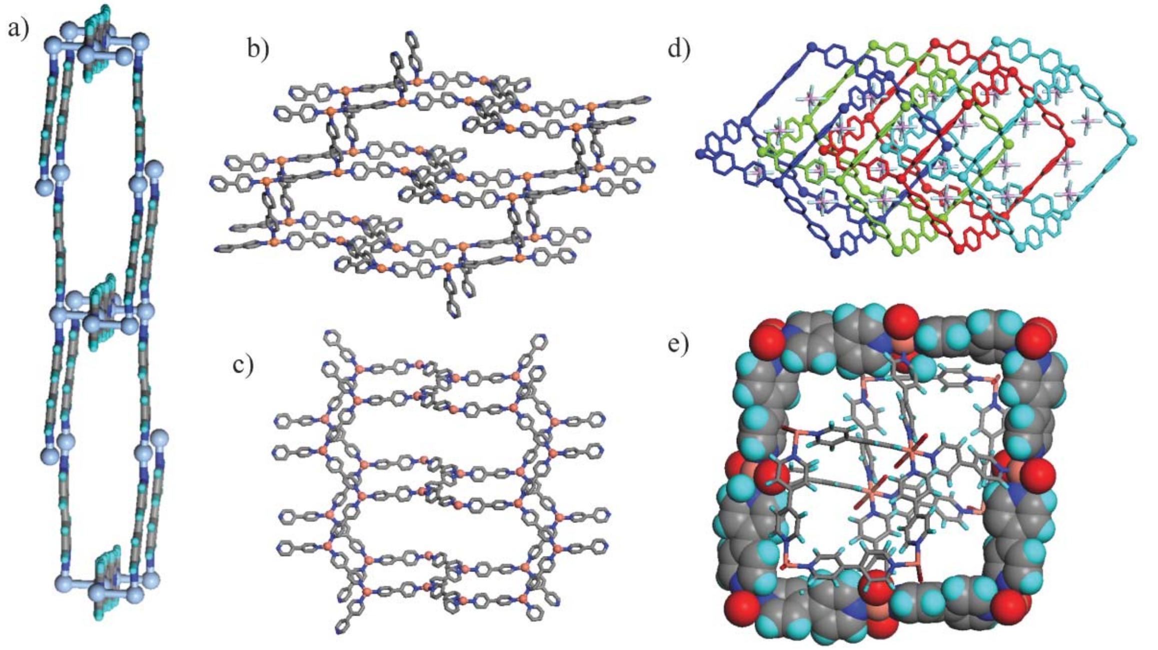


Fig. 8 Illustration for three-dimensional networks: (a) Lincoln Logs network; (b) a 3D framework in which the metal adopts a T-shape geometry; (c) 3D framework with metal atom adopting triangular geometry; (d) 4-fold interpenetration of diamondoid networks; (e) 3D network with $4^2{\cdot}8^2$ topology, the part of the network that is in the plane was shown in space-filling mode for the sake of clarity.

Networks propagated by 4-connected nodes. One of the most popular 4-connected 3D network is the diamondoid network. Such a network using bipy was reported by two groups simultaneously in 1994.[9b,33] Zaworotko *et al.* reported diamondoid networks by treating bipy with $[Cu(CH_3CN)_4]PF_6$. In this structure Cu(I) acts as a tetrahedral node and the bipy acts as a spacer to form the diamondoid network and four of these networks self interpenetrate to fill up the big empty space in the network (Fig. 8d), whereas Ciani *et al.* were able to achieve the similar results by using $Ag(CF_3SO_3)$ instead of the Cu(I) salt. In this structure also, four diamondoid networks interpenetrated to fill up the big cavities in the network. Recently another 4-connected 3D network was reported by Lu *et al.* This network can be generated by opening the some of the connections in square grid network and was described as having $4^2{\cdot}8^2$ topology (Fig. 8e).[34]

Linking square grids through anions. Zaworotko and Subramanian found that the SiF_6 anions act as linkers between square grid networks of bipy and Zn(II) in order to form a three-dimensional network with large channels (Fig. 9).[35a] Subsequently, Kitagawa *et al.* have studied the porosity of these architectures by preparing similar structures but using a Cu(II) salt instead of Zn(II).[35b] These structures have channels with effective dimensions of about 8 × 8 Å which are filled with solvent water molecules. The powder X-ray diffraction studies have shown that the network is stable even after removal of the encapsulated water molecules. The guest removed material was analyzed for methane adsorption/readsorption in the pressure range of 0–36 atm at 298 K. The adsorption/readsorption followed the same isotherm indicating that the channel structure retained throughout this process. At 36 atm the density of adsorbed methane ($0.21\ g\ mL^{-1}$) was found to be almost same as that of compressed methane ($0.16\ g\ mL^{-1}$) at 300 K and 280 atm and indicative of effective filling of the channels of the 3D network. Furthermore, the quantity of methane adsorbed is much higher than that of the conventional zeolite 5A which is known to be the highest adsorber of methane .

Polymers of bipy when the anions are halide ions

Halide ions have several coordination modes with transition metal atoms. They are capable of coordinating to metal in a monodentate fashion similar to nitrates or to bridge the metal atoms in μ_2 and μ_3 modes.

The monodentate coordination of halide ions to transition metals is similar to nitrate's and leads to the formation of

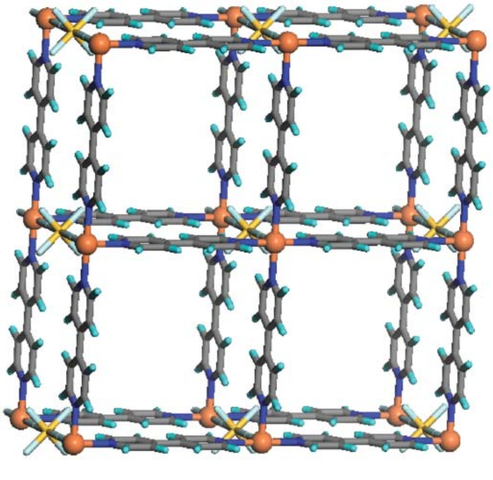


Fig. 9 3D cubic network by linking square grids of Zn(II) and bipy by SiF_6 anions.

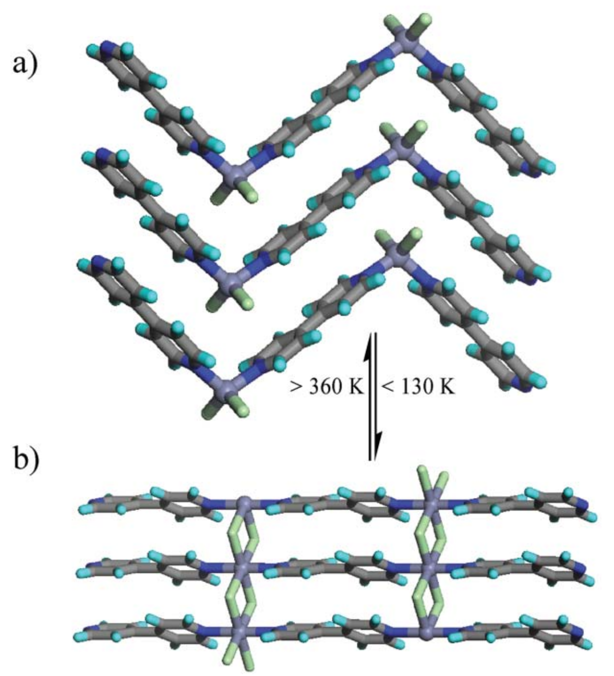
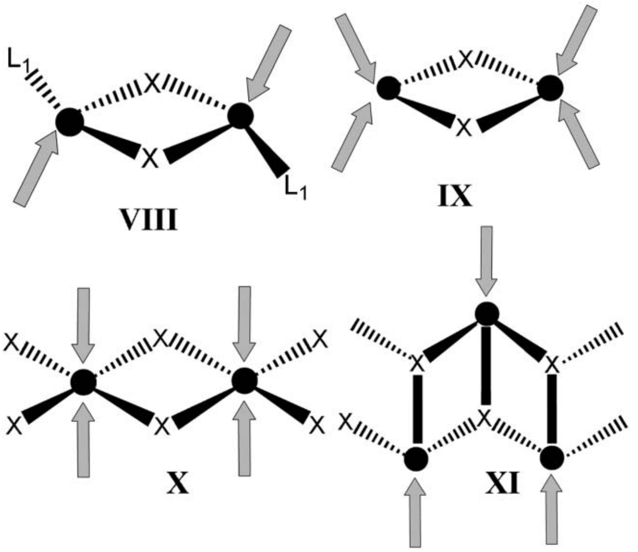


Fig. 10 (a) 1D chain and (b) 2D layer with coordination mode **X** was shown to be interconverted in a crystal-to-crystal fashion.

linear chains with Co(II) (octahedral) or Cu(II) (square planar).[36] However the coordination geometry for zigzag chains differs from those of nitrates as the metal atom adopts a tetrahedral geometry with the coordination of two halide ions (Hg(II) or Zn(II)) and two bipy units.[37] Recently, these types of 1D chain were shown to transform into 2D layers in a crystal-to crystal fashion (Fig. 10).[37a]

To date several metal halide clusters were shown to propagate various coordination polymers with many other ligands. However with bipy only four types of metal-halide (**VIII–XI**) clusters were found to engage in the formation of coordination polymers (Scheme 3).

Formation of 1D chains has been observed frequently by coordination mode **VIII**, in which each metal center (Ag(I) or Cu(I)) coordinates to one bipy, one monodentate ligand (*e.g.* Ph$_3$P, (PhO)$_3$P) and two halide ions (Fig. 11a).[38] The metal clusters **IX**, **X** (most frequent) and **XI** were found to form 2D networks. The cluster **IX** was shown to form by three halide salts (Cl$^-$, Br$^-$ and I$^-$) of Cu(I).[39] These clusters are connected by bipy units to form a honeycomb network with big cavities which are filled by self interpenetration of the networks (Fig. 11b). While the cluster **X** was found to form most frequently for M(II) salts of halides (F$^-$, Cl$^-$, Br$^-$ and I$^-$). In these clusters the metal ion adopts an octahedral geometry where the halide ion bridges the metal atoms in μ_2 fashion (Fig. 10).[40] In these 2D layers the bipy units are arranged such that they are close enough to have good π–π interaction with each other and hence no cavities or guest inclusion resulted. The cluster **XI** was also shown to form by Cu(I) salts of halides (Cl$^-$ and Br$^-$) which are linked further by bipy units to form corrugated 2D networks (Fig. 11c).[39c] Here, unlike the other three clusters, the halide ions bridges the metals in a μ_3 fashion.



Scheme 3 Bimetallic (**VIII–IX**) and polymetallic clusters (**X–XI**) by halide ions.

Polymers of bipy when the anions are carboxylates

When carboxylates are the anions, the design of coordination polymers of bipy is relatively unpredictable due to the

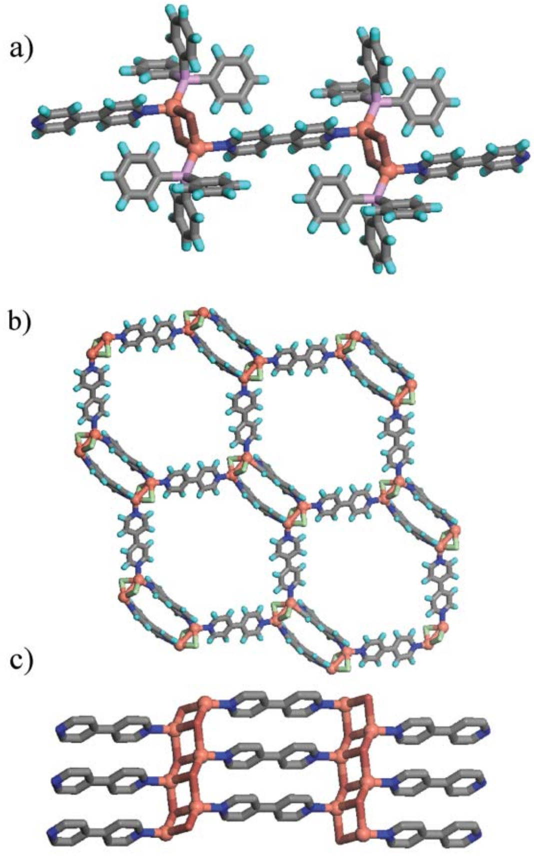


Fig. 11 Illustrations for polymers containing metal halide clusters (a) linear chain which is formed by **VIII** (notice the PPh$_3$ ligand); (b) honeycomb network which is formed by cluster **IX**; (c) corrugated 2D layer which contains **XI**.

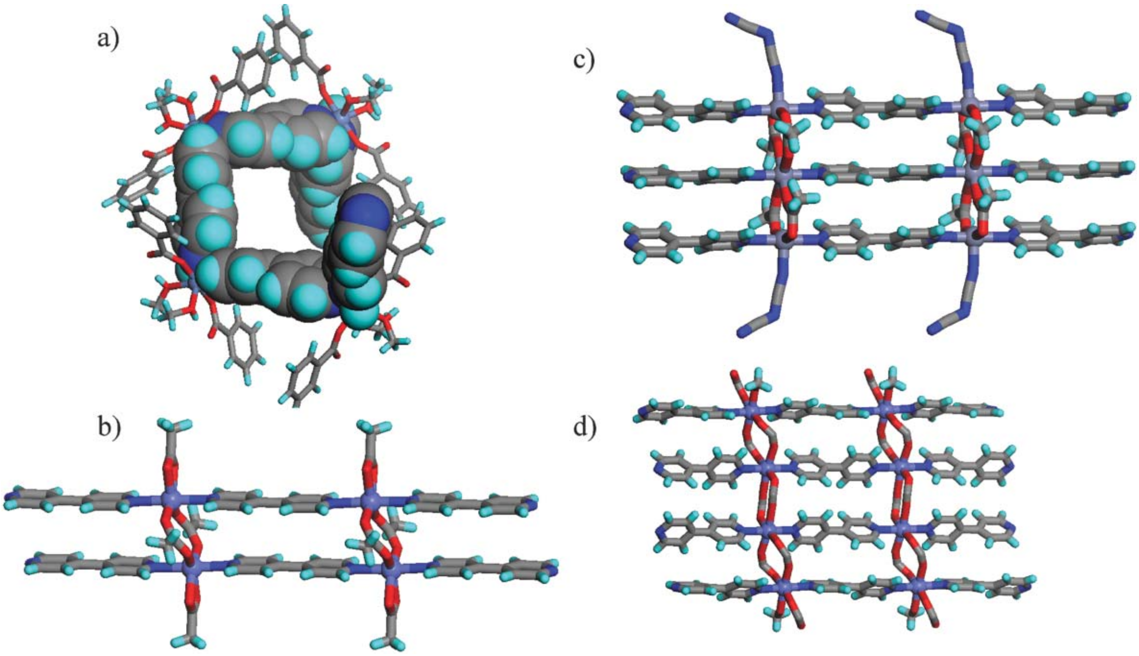


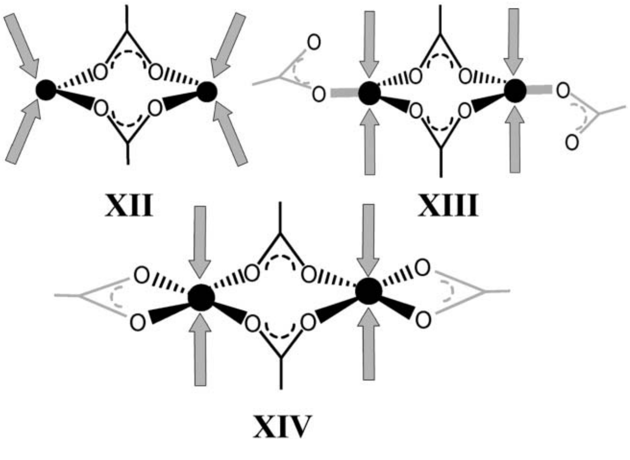
Fig. 12 Illustration for coordination polymers of bipy when carboxylates are anions: (a) four-fold helix, bipy units were shown in space-fill mode and benzoates MeOH were shown in cylinder mode; (b) double chain (**XIV**); (c) triple chain; (d); quadruple chains.

unpredictable coordination modes of carboxylates with transition metals. In some cases, carboxylates may exhibit similar coordination modes as nitrates with transition metals to form linear,[41] zigzag,[42] ladder[43] and square grids networks.[41f] In addition to those networks, helices,[44] double,[45] triple[46] and quadruple[41a] chains were discovered when the anions are carboxylates. Helices were observed when bipy and benzoic acid were reacted with $Ni(CH_3COO)_2$. These chiral helices exhibited four-fold symmetry as each coil of the helix contains four residues of bipy with a pitch length of 27 Å (Fig. 12a). The packing of the helices *via* aromatic and C–H···O interactions generates chiral cavities that are occupied by the dimers of nitrobenzene. The disruption of aromatic interactions between bipy and benzoate, by introducing an –OH group at the *o*-position of benzoic acid resulted in linear coordination polymer. Interestingly, these linear coordination polymers pack in a trigonal fashion (chiral) rather than in parallel fashion.

Furthermore, the bridging ability of the carboxylates with transition metals leads to the formation of bimetallic, trimetallic and tetrametallic clusters which will be further connected by bipy to form double, triple and quadruple chains respectively. The bimetallic cluster has been shown to form in three ways **XII**, **XIII** and **XIV** (Scheme 4). The cluster **XII** was observed with Ag(I) in one structure and the cluster **XIII** was observed with Cu(II) in three structures. Whereas the cluster **XIV** is more frequent (7 structures) and observed with Co(II), Zn(II) and Ni(II). The trimetallic and tetrametallic clusters were shown to form with Zn(II) and Co(II) respectively.

Conclusions and future outlook

A simple rod like *exo*-bidentate ligand 4,4′-bipyridine was described as a prototypical bridging ligand for several transition metals. The network geometries were discussed to depend on coordination geometry of the metals, coordination of anions, metal to bipy ratios and guest molecules. The polymers of bipy with transition metals include linear chains, zigzag chains, double, triple and quadruple chains, ladders, molecular antennas, railroads, four-fold helices, bilayers, square grids, rectangular grids, Lincoln Log, 3D frames, $4^2 \cdot 8^2$, diamondoid and cubic geometries. In these polymers, linear chains were found to be well populated particularly when the anion is carboxylate (37 out of 97 linear chain structures). Whereas the population of zigzag chains is more in the presence of ClO_4^- (nine structures) and carboxylates (eight structures). Furthermore, ladder structures are more frequent when the anions are nitrates (seven structures) or carboxylates (four structures). Two-dimensional networks such as bilayer (12 structures) and square grids (16 structures) are most populated when the anions are nitrates. The dependence of



Scheme 4 Three types of bimetallic clusters formed by carboxylates.

network geometries on the anions was beautifully illustrated by Kitagawa *et al.* by studying series of anion exchange reactions.[26f] These studies shows that interconversions between 1D chains, 2D open square grids, interpenetrated square grids and cubical networks are possible by exchange of anions. Some more studies are needed in this direction to fully understand their role. Concerning the guest inclusion the square grid structures and a 3D network were shown to include large guest molecules. Ladders and bilayers exhibited a tendency to include small solvent molecules such as EtOEt, CH_3CN, $CHCl_3$, MeOH, H_2O, DCM, DMF and THF. As an exception, one ladder structure was shown to include a big molecule such as pyrene. If the existence of number of structures relates to the ease of formation of the polymer, the order of formation of some of these networks can be shown as linear chain (97 structures) > square grid (38 structures) > zigzag (26 structures) > bilayer (16 structures) > ladder (12 structures). Further, the modified ligands of bipy were already shown to exhibit some more newer topological networks than bipy. Those studies hint that many more novel topological networks, known or unknown, remain to be explored with bipy. For example in 1D networks, helices of bipy having other than 4-fold axis are possible. Furthermore, already known 2D networks such as brick-wall and herring-bone types remain to be explored with bipy. In 3D networks the number of examples are very limited, although bipy was shown to form five types of topological networks.

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