Coordination driven architectures based on metalloligands offering appended carboxylic acid groups

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Abstract. The field of coordination polymers (CPs) has grown rapidly in the recent time and exemplifies one of the most exciting fields in the solid state and structural chemistry. In order to search for new CPs with desirable structural features and attractive functional properties, various synthetic strategies have been adopted including the challenging metalloligand approach. This approach relies on developing a metalloligand that is capable of placing the appended functional groups to limited directions thus resulting in limited structural variations—a landmark step towards predictable architectures. Consequently, a variety of metalloligands offering assorted functional groups have been developed and explored for the construction of noteworthy CPs. This perspective article summarizes an important class of metalloligands offering appended carboxylic acid groups with a focus on the design strategies to understand the architectures of the resultant CPs being controlled by the metalloligands. In addition, a concise discussion has been included about the applications of selected CPs to demonstrate their practical utilization.

Keywords. Metalloligand; carboxylic acid; coordination polymer; framework material; designer material.

1. Introduction

The field of coordination polymers (CPs) has grown rapidly in the last decade and exemplifies one of the most exciting fields in solid state and structural chemistry.^{1–4} The spectacular variety of their structures and properties, facile structural-modulation as well as versatile applications has significantly fascinated the scientific community.^{2–6} Therefore, CPs represent promising new class of porous crystalline solid materials with noteworthy applications including gas storage,^{7–10} separation,^{11–13} sorption,^{14–16} ion-exchange,^{17,18} proton conduction,^{19–21} sensing,^{22–24} catalysis,^{25,26} drug delivery^{27,28} and other bio-medical functions.²⁹ In order to search for new CPs with desirable structural features and notable functional properties, various synthetic strategies have been developed.³⁰ Over the years, the most common synthetic strategy has been to use a suitable multi-topic organic ligand that functions as a linker in conjunction with a metal ion.³¹ The appropriate reac-

tion of the two gives rise to a variety of CPs with a variety of architectures. Despite considerable progress using this synthetic strategy, predicting a new and particular type of CP remains a daunting challenge.³² Such a difficulty is associated with controlling following parameters that potentially regulate the self-assembly process of a CP: an organic ligand and its denticity, nature of a ligand (neutral versus charged), a metal ion and its geometrical preferences, metal-to-ligand ratio, solvent, associated anions, reaction temperature, etc.³³ Most often, both selection of a metal ion and an organic ligand remain the key features to achieve the desirable architecture with potential functional properties.³⁴

The second, less-common yet powerful, synthetic strategy is to use a metalloligand in place of an organic ligand in conjunction with a secondary metal ion to arrive at a desirable architecture.¹ This approach relies on developing a metalloligand that is capable of placing the appended functional groups to limited directions and therefore such functional groups can bind to the secondary metal ions in limited geometrical manner.^{35–37} As a result of structural rigidity being offered by a metalloligand, the resultant CPs are often structurally predictable—a landmark step towards predictable

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Figure 1. Synthetic route and structure of CP **1a** showing coordination of metalloligand **1** with Cu^{2+} ions; adapted from ref. ⁴².

architectures.^{1,35–37} There are several other advantages with the metalloligand approach: (i) this strategy allows selecting a primary metal ion (within a metalloligand) in addition to a secondary metal ion and as a result offers easy access to heterometallic CPs; (ii) facile selection of both primary and secondary metals allows placing desirable metals in close proximity; (iii) facile selection of secondary metals allows choices over desirable *d*-block as well as *f*-block elements.

Using the metalloligand approach, a variety of CPs with novel structural features and applications have been developed.^{1,6} A large number of metalloligands have been synthesized and utilized for the preparation of diverse CPs. A metalloligand can be conveniently classified based on the type(s) of functional groups being offered for coordinating to the secondary metal ions.¹ The types of functional groups that one can think of are essentially endless. However, the most common functional groups that are being offered by a metalloligand are heterocyclic rings (mostly pyridine)¹ and carboxylic acids.^{35–38} A significant amount of work has been done as well as reviewed for the metalloligands offering appended heterocyclic rings,¹ particularly pyridine and therefore this article will not cover such metalloligands and their CPs. This perspective summarizes a variety of metalloligands offering appended carboxylic acid groups with a focus on the design strategies to understand the architectures of the resultant CPs. However, a concise discussion has been included about the notable applications of some of the CPs to demonstrate their practical utilization.

2. Coordination polymers based on metalloligands

This section illustrates selected metalloligands offering appended carboxylic acid groups that have been utilized for the subsequent construction of noteworthy coordination polymers. The metalloligands have been organized based on the chelating ligands that coordinate to the primary metal ion thus constituting a metalloligand.

2.1 Coordination polymers based on porphyrin-based metalloligands

Among various metalloligands, the widest applied ones are metalloporphyrins (MPs).^{39,40} By integration of different peripheral functional substituents on a porphyrin ring, MPs can offer interesting coordinating abilities to secondary metals. Therefore, use of MPs as the metalloligands allows facile structural modification and thus design possibilities.⁴¹ Since a variety of metals can be inserted into a porphyrin ring, a large number of MPs are possible without significantly altering the porphyrin-based framework structure. Moreover, utilization of MPs as the metalloligands provides ample opportunities to focus on the photochemical, redox, and catalytic properties of the resultant CPs.^{39–41}

Mori and co-workers⁴² have synthesized a porphyrin-based CP $[\text{Cu}_2(\mathbf{1})]$ (**1a**) using metalloligand **1** offering two appended aryl dicarboxylic acid groups (Figure 1). Crystallographic analysis revealed **1a** as a three-dimensional (3D) network consisted of a large internal spherical cavity diameter of ca. 20 Å. The internal cavity was surrounded by a total of 16 accessible metal sites with two distinct metals: eight Zn(II) ions from metalloligands and eight Cu(II) ions from $[\text{Cu}_2(\text{OOCR})]$ based paddlewheel secondary building units

Figure 2. (a) Synthetic route for CP **2a**; (b) Structure of **2a** showing coordination of metalloligand **2** with Co^{2+} ions. (c) Oxidation of *trans*-stilbene catalyzed by **2a** resulting in the formation of stilbene-oxide. Adapted from ref. ⁴³.

(SBUs). **1a** offered ca. 8 Å pore windows along the *a*- and *b*-axes and ca. 7 Å windows along the *c*-axis. N_2 and H_2 gas adsorption measurements were performed at 77 K while H_2 uptake was found to be ca. 0.81 wt% corresponding to the pore volume of 0.204 $\text{cm}^3 \text{g}^{-1}$.

Ma and co-workers⁴³ have solvothermally synthesized a polyhedral cage-based CP $[\text{Co}_2(\text{2})(\mu^2\text{-H}_2\text{O})(\text{H}_2\text{O})_4]$ (**2a**) that offered a high density of about five catalytically active cobalt ions per nm^3 (Figure 2). The permanent porosity in **2a** was confirmed by CO_2 adsorption at 273 K which exhibited a surface area of ca. 750 $\text{m}^2 \text{g}^{-1}$. **2a** was used as an efficient catalyst for the epoxidation of *trans*-stilbene using t-BuOOH maintaining good selectivity. The turnover frequency (TOF) of 69 h^{-1} was observed in first 12 h which was due to the high density of cobalt centres in **2a**. Such catalytic results demonstrated superior performance in the context of both selectivity and overall conversion in the catalytic epoxidation of *trans*-stilbene.

One of the most widely used porphyrins for constructing CPs is tetrakis(4-carboxyphenyl)porphyrin.⁴⁴ Zhou and co-workers⁴⁵ demonstrated a highly stable mesoporous CP **3a** which offered large 1D open channels (Figure 3). **3a** was constituted of Fe-porphyrins connected to Zr-based SBUs and showed exceptionally high stability even in conc. HCl. The porosity of **3a** was examined by N_2 adsorption isotherm at 77 K. **3a** acted as an effective peroxidase mimic with both excellent substrate binding affinity (K_m) and catalytic activity

(k_{cat}) in aqueous media and also catalyzed the oxidation of a variety of substrates with special emphasis on pyrogallol. The excellent catalytic performance was attributed to the high density of porphyrin centres in **3a**. The catalytic reaction, monitored by the absorption spectroscopy, followed the enzymatic Michaelis–Menten pathway. The active sites were located on the inner wall of an open channel with a diameter of 3.7 nm and showed notable activity for the oxidation of various substrates. **3a** fulfilled requirements for a biomimetic catalyst by illustrating large pore size, exceptionally high water stability, and potentially catalytically active centres.

Wu and co-workers⁴⁶ demonstrated synthesis of four porphyrin-based CPs by reacting metalloligands **4** or **5** with $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Zn}$ and Cd) (Figure 4). The 3D isomorphous **4a** and **4b** were constituted of metalloligands connected to four $[\text{M}_2(\text{OOCR})_4]$ ($\text{M} = \text{Zn}$ or Cd) paddle-wheel SBUs and a formate pillar. The formate pillar connects with $[\text{M}_2(\text{COOR})_4]$ SBUs and porphyrin- Mn^{3+} in a non-interpenetrated AB stacking pattern resulting in a 3D network. Both **4a** and **4b** exhibited two types of channels with dimensions of $7.74 \times 11.79 \text{ \AA}^2$ and $11.79 \times 11.79 \text{ \AA}^2$, respectively. Although **4a** and **4b** offered void space corresponding to 61 and 64%, respectively, blocked axial coordination sites on Mn ions by the formate pillars made them inaccessible to the substrates. If Mn was replaced by Fe in the porphyrin, the formate pillar homogeneously linked two $[\text{Zn}_2(\text{OOCR})_4]$ paddle-wheel SBUs to form an AA stacked 3D network **5a**.

Figure 3. (a) Synthetic route and structure of CP **3a**. (b) Peroxidase-like oxidation of pyrogallol catalyzed by **3a**. Adapted from ref. ⁴⁵.

Figure 4. (a) Synthetic route for CPs **4a–5b**. (b) Structure of **4a** showing coordination of metalloligand **4** with Zn^{2+} ions. (c) Structure of **4b** showing coordination of metalloligand **4** with Cd^{2+} ions. (d) Structure of **5a** showing coordination of metalloligand **5** with Zn^{2+} ions. (e) Structure of **5b** showing coordination of metalloligand **5** with Cd^{2+} ions. (f) Aldol reaction of aldehydes and ketones catalyzed by CPs **4a–5b**. Adapted from ref. ⁴⁶.

Figure 5. (a) Synthetic route for CPs **6a–9a**. (b) Structures of **6a–8a** showing coordination of metalloligands **6–8** with Pb^{2+} ions. (c) Structure of **9a** showing coordination of metalloligand **9** with Pb^{2+} ions. Adapted from ref. ⁴⁸.

5a consists of two kinds of channels throughout the network with dimensions of $8.86 \times 16.67 \text{ \AA}^2$ and $11.81 \times 11.81 \text{ \AA}^2$, respectively, and having ca. 67% void space. With $\text{Cd}(\text{NO}_3)_2$, metalloligand **5** acted as a pentadentate unit in the resultant CP and ligated five Cd(II) ions via $[\text{Cd}_2(\text{OOCR})_4(\text{H}_2\text{O})_6]$ SBUs, despite the fact that one of the carboxylate groups was protonated. Moreover, two Fe-based metalloligands were bridged by a μ^2 -O group in this case.⁴⁷ **5b** offered ca. 49% void space for the solvent molecules. These CPs exhibited interesting catalytic properties for the epoxidation of olefins, oxidation of cyclohexane, and intermolecular aldol reaction of aldehydes and ketones. Although all CPs were permanently porous, substrate molecules were inaccessible to the porphyrin-bound metals due to the ligated formate pillars. Hence, catalytic properties were due to the secondary metals on the exterior surface with excellent conversion and selectivity. In CPs **5a** and **5b**, Fe^{3+} ions in metalloligands were readily accessible to substrates but they were not stable under the epoxidation conditions. Therefore, **5a** and **5b** were used for the catalytic intermolecular aldol reaction of aldehydes and ketones with excellent substrate conversions.

Wu and co-workers⁴⁸ have reported several porphyrin-based metalloligands (M = Co^{2+} (**6**), Ni^{2+} (**7**), Cu^{2+} (**8**)

and V^{4+} (**9**)) which on reaction with $\text{Pb}(\text{NO}_3)_2$ afforded the respective CPs: $\text{Pb}_2(\mathbf{6})(\text{H}_2\text{O})(\text{DMF})$ (**6a**), $[\text{Pb}_2(\mathbf{7})(\text{H}_2\text{O})(\text{DMF})]$ (**7a**), $[\text{Pb}_2(\mathbf{8})(\text{H}_2\text{O})(\text{DMF})(\text{H}_2\text{O})]$ (**8a**) and $[\text{Pb}_2(\mathbf{9})(\text{H}_2\text{O})_2]$ (**9a**) (Figure 5). Diffraction studies revealed that such CPs differed in framework topologies and porphyrin configuration that varied from flat to wavy to bowl-shaped. The porphyrin core played a significant role by controlling the stacking nature of metalloligands and the coordination spheres of the Pb^{2+} ions in the resultant CPs. In isomorphous **6a**, **7a** and **8a**, octa-coordinated Pb^{2+} ions were alternately bridged by two and three $\text{O}_{\text{carboxylate}}$ atoms and consisted of 1D open channel of $13.2 \times 6.7 \text{ \AA}^2$ dimensions. Interestingly, porphyrin ring adopted a saddle-like twisted conformation with a mean deviation of ca. $0.24 \text{ \AA}$. PLATON calculations exhibited void spaces of 25.8, 24.4 and 25.8% in **6a**, **7a** and **8a**, respectively. In case of **9a**, 3D framework offered two kinds of 1D channels throughout the network with dimensions of ca. $9.0 \times 8.9 \text{ \AA}^2$ and ca. $15.3 \times 6.1 \text{ \AA}^2$. In **9a**, the vanadium atom is out of the porphyrin plane with a mean deviation of ca. $0.50 \text{ \AA}$ while it offered void space of ca. 35%. Fluorescence spectra for all four CPs in the solid state at room temperature displayed intense luminescence bands in the range of 370–520 nm. The fluorescent spectral studies suggested

Figure 6. (a) Synthetic route for CPs **10a**, **11a** and **10b**. (b) Structure of **10a** showing coordination of metalloligand **10** with Mn^{2+} ions. (c) Structure of **11a** showing coordination of metalloligand **11** with Mn^{2+} ions. (d) Structure of **10b** showing coordination of metalloligand **10** with Cd^{2+} ions. (e) Selective oxidation of alkyl benzenes catalyzed by CPs **10a**, **11a** and **10b** using $tBuOOH$. Adapted from ref. ⁴⁹.

that the emission of these CPs depended on the framework structures while they were insensitive to the porphyrin core.

Wu and workers⁴⁹ have further constructed porous porphyrin-based frameworks by the reaction of octatopic porphyrin based metalloligands **10** and **11** with secondary metals (Figure 6). The resulting 3D CPs $[Mn_5Cl_2(\mathbf{10})(DMF)_4(H_2O)_4]$ (**10a**), $[Mn_5Cl_2(\mathbf{11})(H_2O)_8]$ (**11a**), and $[Cd_5Cl_2(\mathbf{10})(H_2O)_6]$ (**10b**) were isostructural as revealed by their crystal structures. These CPs offered inter-crossed pore windows of ca. 11.5 Å and pore cages of ca. 21.3 Å. The structures were constituted of octatopic metalloligands (**10** or **11**) connected to two metal-containing SBUs; binuclear $[Mn_2(OOCR)_4]$ and trinuclear $[Mn_3(OOCR)_4(\mu-H_2O)_2]$. PLATON calculations exhibited that these CPs presented ca. 60% void space which encapsulated many solvent molecules. The accessibility of substrates through these pores was examined by the sorption studies. The catalytic activities for these frameworks for the oxidation of alkyl-benzenes were examined using $tBuOOH$ as an oxidant. Results indicated that **10a** was much superior to **10b** and **11a**, exhibiting efficient and selective oxidation

of ethylbenzene to acetophenone in over 99% yield with a turnover number (TON) of 8076 after 48 h.

Ma and co-workers⁵⁰ have reported a porous porphyrin-based framework $[Co_3(\mathbf{12})(OH)(H_2O)_4]$ (**12a**) that has been constructed from octatopic porphyrin metalloligand **12** (Figure 7). In **12a**, metalloligand **12** was connected to the distorted cobalt trigonal prism based SBUs producing highly porous and robust CP with a high surface area of 2037 m² g⁻¹. **12a** showed permanent porosity with ca. 60% solvent accessible voids and interesting CO₂ capture performance. The high surface area of **12a** was further confirmed by N₂ adsorption at 77 K and O₂ adsorption at 87 K, both of which revealed similar surface area. The CO₂ adsorption isotherm measured at 273 K indicated that **12a** has an uptake capacity of ca. 33 wt% at 760 Torr.

Using similar metalloligands **13** and **14**, Ma and co-workers⁵¹ have constructed CPs $[Zn_{19}(\mathbf{13})_3(NO_3)_8]$ (**13a**) and $[Cd_{11}(\mathbf{14})_3(H_3O)_8]$ (**14a**) (Figure 8). The network was constituted of metalloligands connected through Zn-/Cd-based SBUs. The crystal structure of **13a** exhibited window dimension of ca. 7.8 × 8.1 Å² with an internal diameter of

Figure 7. Synthetic route and structure of CP **12a** showing coordination of metalloligand **12** with Co^{2+} ions; adapted from ref.⁵⁰.

Figure 8. (a) Synthetic route for CPs **13a** and **14a**. (b) Structure of **13a** showing coordination of metalloligand **13** with Zn^{2+} ions. (c) Structure of **14a** showing coordination of metalloligand **14** with Cd^{2+} ions. Adapted from ref.⁵¹.

21.5 Å. Similarly, **14a** displayed window dimension of ca. $8.0 \times 8.2 \text{ Å}^2$ and an internal diameter of 22.5 Å. Both **13a** and **14a** were permanently porous and offered high solvent accessible volumes of ca. 70% and ca. 76%, respectively. **13a** was subjected to CO_2 uptake studies and CO_2 adsorption isotherm

at 273 K exhibited high uptake capacity of $124 \text{ cm}^3 \text{g}^{-1}$ (ca. 24 wt%).

Zhang and co-workers⁵² have synthesized an anionic In-porphyrin based CP **15a** through solvothermal reaction (Figure 9). Interestingly, six porphyrin-based metalloligands

Figure 9. Synthetic route and structure of CP **15a** showing coordination of metalloligand **15** with In^{3+} ions; adapted from ref. ⁵².

Figure 10. (a) Synthetic route for CP **16a**. (b) Structure of **16a** showing coordination of metalloligand **16** with Gd^{3+} ions. (c) Epoxidation of *trans*-stilbene with O_2 catalyzed by **16a**. Adapted from ref. ⁵⁴.

15 connected eight $[\text{In}(\text{OOCR})_4]^-$ SBUs to form a rare Williams- β -tetrakaidecahedral cage consisted of 14 faces, 24 vertices, and 36 edges. Because of the presence of anionic SBUs, **15a** formed an anionic framework. **15a** was highly porous due to the large internal dimensions of the cage ($33 \times 23 \times 23 \text{ \AA}^3$) and the presence of hexagonal ($19 \times 16 \text{ \AA}^2$) and pentagonal ($17 \times 13 \text{ \AA}^2$) windows. **15a** exhibited excellent photo-catalytic activity towards the selective oxygenation of sulphides which was tunable by indium metallation.

2.2 Coordination polymers based on salen-based metalloligands

Salen platform has been one of the most studied ligands for coordination as well as substrate oxidation chemistry.⁵³ The easily accessible salen-based ligands, their ability to

coordinate a variety of metal ions and their structural tunability has been the landmark features responsible for their remarkable growth.⁵³ Such structural and coordination features have attracted both supramolecular and material chemistry communities alike to incorporate salen-based fragment in their design. The most common modification is to incorporate a suitable ligating group to the salen-skeleton to make it suitable as a metalloligand and carboxylic acid group has been quite successful in this regard.

Roesky and co-workers⁵⁴ have reported that salen-based metalloligand **16** on reaction with $\text{Gd}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_n$ resulted in the formation of 1D CP $[\text{Gd}_2(\text{16})_2(\text{NO}_3)_2(\text{DMF})_5]_n$ (**16a**) (Figure 10). In this CP, two neighbouring Gd atoms are connected through four $\text{O}_{\text{carboxylate}}$ groups from four Mn-salen units. Each Gd atom is eight-coordinated; four O-atoms from bridging carboxylate groups of the Mn-salen units, two O-atoms from a bidentate nitrate group, and two O-atoms

Figure 11. (a) Synthetic route and simplified chemical drawing of CP **17a**. (b) Sequential epoxidation followed by ring-opening reaction of alkene catalyzed by **17a**. Adapted from ref.⁵⁵.

from two ligated DMF molecules. Herein, two Mn–salen units form two orthogonal wave-shaped scaffolds. **16a** was used as a remarkable catalyst in the liquid-phase epoxidation of *trans*-stilbene with molecular oxygen producing stilbene oxide. The influence of solvent, catalyst concentration, reaction temperature, oxidant, and oxidant flow rate on conversion, yield, and selectivity was analyzed. A conversion of up to 70% (88% selectivity), and a TON of 84 were observed after 24 h.

Cui and co-workers⁵⁵ have demonstrated the synthesis of CP $[Zn_4O(17)_3]$ (**17a**) using salen-based metalloligand **17** (Figure 11). Six bidentate carboxylate groups from six metalloligands coordinated to four Zn(II) ions to generate $[Zn_4(\mu^4-O)(OOCR)_6]$ SBUs. A combination of metalloligands and SBUs produced a 3D network. Two-fold interpenetration in the resultant network helped bringing the pair of Cu(salen) units into close proximity with Cu–Cu distance of ca. 8.2 Å. Such a fact created an excellent platform to engineer heterogeneous catalysis *via* cooperativity leading to improved chemical activity and enantio-selectivity. **17a** was used as an efficient and recyclable heterogeneous catalyst for a variety of asymmetric sequential alkene epoxidation (using PhIO) followed by ring-opening reactions (RORs) using water, finally producing asymmetrical diols.

Cui and co-workers⁵⁶ have demonstrated chiral nanoporous CPs constructed by using chiral Ni–salen (**18**) and Co–salen (**19**) metalloligands (Figure 12). Heating a mixture of $Cd(NO_3)_2 \cdot 6H_2O$ with **18** and **19** afforded CPs $[Cd_4(18)_4(DMF)_4]$ (**18a**) and $[Cd_4(19)_4(DMF)_4(OAc)_4]$ (**19a**). In **18a**, tetrameric $[Cd_4(OOCR)_8]$ SBUs were formed by six bidentate and two tridentate carboxylate groups. Each SBU in **18a** is linked to eight Ni–salen metalloligands (**18**) whereas every Ni–salen metalloligand is linked to three Cd(II) ions to generate a chiral 3D framework having channels with cross sections of ca. $1.2 \times 0.8 \text{ nm}^2$. CP **19a** is isostructural to **18a** and presented a similar porous 3D network with open channels of ca. $1.2 \times 0.8 \text{ nm}^2$. PLATON calculation

showed that both **18a** and **19a** presented ca. 44% of the total volume available for guest inclusion. CP **19a** was shown to be an efficient recyclable heterogeneous catalyst for the hydrolytic kinetic resolution (HKR) of racemic epoxides with up to 99.5% enantiomeric excess (ee). The structure of **19a** placed Co–salen units into a highly dense arrangement and close proximity that enhanced the bimetallic cooperative interactions leading to improved catalytic activity and enantio-selectivity. The solid catalyst was recycled and reused without any notable loss of catalytic activity and enantio-selectivity. The high tunability of metallo-salen based CPs projected an opportunity to develop a library of chiral catalysts with practically useful enantio-selectivity.

Jiang and co-workers⁵⁷ have reported a novel 3D chiral framework $[Cd_4Cl(20)_3(20-HL)(H_2O)_6(DMF)]$ (**20a**) based on metalloligand **20** and tetranuclear SBUs $[Cd_4Cl(OOCR)_7(CO_2H)]$ (Figure 13). **20a** displayed a nano-porous framework where each tetranuclear SBU was linked by eight Ni–salen units whereas each Ni–salen unit was connected to two tetranuclear SBUs to generate a 3D architecture with open channels. **20a** offered open chiral channels with cross sections of ca. $1.1 \times 0.9 \text{ nm}^2$ whereas PLATON calculation confirmed ca. 26% of void space available for substrate inclusion. Considering good stability, permanent porosity and Lewis acidic sites; **20a** was used as the heterogeneous catalyst for the asymmetric cycloaddition of CO_2 under relatively mild reaction conditions producing optically pure propylene carbonate. **20a** was a recyclable and reusable catalyst and retained its framework structure after being used for several times.

Lin and co-workers⁵⁸ have reported related chiral CPs $[Zn_4(21)_3(\mu^4-O)]$ (**21a**), $[Zn_4(22)_3(\mu^4-O)]$ (**22a**) and $[Zn_4(23)_3(\mu^4-O)]$ (**23a**) constituted of metalloligands **21**–**23** and $[Zn_4(\mu^4-O)(OOCR)_6]$ SBUs (Figure 14). The channel sizes in these CPs were systematically tuned by introducing spacers of different lengths that were derived from chiral Mn-salen metalloligands. In **21a**, carboxylate

Figure 12. (a) Synthetic route for CPs **18a** and **19a**. (b) Structure of **18a** showing coordination of metalloligand **18** with Cd^{2+} ions. (c) Structure of **19a** showing coordination of metalloligand **19** with Cd^{2+} ions. (d) Hydrolytic kinetic resolution reaction of terminal epoxides catalyzed by **19a**. Adapted from ref. ⁵⁶.

Figure 13. (a) Synthetic route for CP **20a**. (b) Structure of **20a** showing coordination of metalloligand **20** with Cd^{2+} ions. (c) Coupling reaction of propylene oxide with CO_2 catalyzed by **20a**. Adapted from ref. ⁵⁷.

groups from six metalloligands **21** coordinated to four Zn centres to form $[\text{Zn}_4(\mu^4 - \text{O})(\text{OOCR})_6]$ SBUs, which resulted in a 3D network. **21a** offered a two-fold interpenetrated

architecture with large dimensions of open channels measuring $0.8 \times 0.6 \text{ nm}^2$ and ca. 61% of void space. Similarly, **22a** consisted of two-fold interpenetrated architecture possessing

Figure 14. (a) Synthetic route for CPs **21a**, **22a** and **23a**. (b) Structure of **21a** showing coordination of metalloligand **21** with Zn^{2+} ions. (c) Structure of **22a** showing coordination of metalloligand **22** with Zn^{2+} ions. (d) Structure of **23a** showing coordination of metalloligand **23** with Zn^{2+} ions. (e) Enantio-selective epoxidation of alkenes catalysed by **21a**, **22a** and **23a**. Adapted from ref. ⁵⁸.

channel sizes of $1.5 \times 0.7 \text{ nm}^2$ amounting to ca. 77% void space. Metalloligand **23**, having even longer appended arms, on reaction with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ resulted in **23a** that adopted a three-fold interpenetrated architecture where two of the three interpenetrating nets were fully occupied and packed closely to each other. **23a** consisted of the open channel of dimensions $1.1 \times 0.8 \text{ nm}^2$ that were intermediate between those of **21a** and **22a**. Importantly, open channel and pore sizes of these CPs vary systematically, depending on the tunable salen units and controllable interpenetration patterns. These CPs functioned as the highly effective catalysts for the enantio-selective epoxidation of a variety of unfunctionalized olefins with up to 92% ee. The epoxidation rates strongly depended on the channel dimensions, providing evidence that larger channels can increase reaction rate by facilitating the diffusion of reactants and products.

2.3 Coordination polymers based on pyridine-amide based metalloligands

Pyridine-amide based ligands have been extensively used in coordination chemistry as they produce stable and structurally-versatile metal complexes.⁵⁹ Such ligands have

attracted great interest in stabilizing metal ions in their higher oxidation states due to the involvement of anionic σ -donating N_{amide} groups.⁵⁹ In contrast, supramolecular chemistry in general and anion-coordination chemistry in particular with such ligands has been significantly successful due to the presence of hydrogen bonding sensitive amide groups.⁶⁰ The pyridine-amide based ligands have also been noteworthy in the synthesis of metalloligands and their resultant CPs and the following examples gratifyingly establish such a fact.

Gupta and co-workers³⁵ have reported the utilization of Co^{3+} complexes **24** and **25** respectively appended with *para*- and *meta*-arylcarboxylic acid groups as the metalloligands (Figure 15). The reaction of **24** and **25** with $\text{M}(\text{OAc})_2$ salt ($\text{M}^{2+} = \text{Zn}$ and Cd) resulted in the formation of CPs $[\text{Zn}_6(\text{24})_2(\text{OH})_2(\text{H}_2\text{O})_{10}]$ (**24a**), $[\text{Cd}_{2.5}(\text{24})(\text{H}_2\text{O})_{10}]$ (**24b**), $[\text{Zn}_3(\text{25})\text{Zn}_3(\text{OH})(\text{H}_2\text{O})_6]$ (**25a**) and $[\text{Cd}_{2.5}(\text{25})(\text{H}_2\text{O})_{15}]$ (**25b**). The molecular structures of all four CPs showed that the Co^{3+} -based metalloligands are connected through $\text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$ ions resulting in 3D networks. Notably, all four CPs showed solvent-accessible voids (SAVs) of different volume and a noticeable difference was observed between the networks generated by *para*- versus *meta*-arylcarboxylate based metalloligands. For example, crystal structures of CPs **24a** and **24b** (both with *para*- arylcarboxylate groups) showed

Figure 15. (a) Synthetic route for CPs **24a**, **24b**, **25a** and **25b**. (b) Structure of **24a** showing coordination of metalloligand **24** with Zn^{2+} ions. (c) Structure of **24b** showing coordination of metalloligand **24** with Cd^{2+} ions. (d) Structure of **25a** showing coordination of metalloligand **25** with Zn^{2+} ions. (e) Structure of **25b** showing coordination of metalloligand **25** with Cd^{2+} ions. (f) Ring-opening reactions of styrene oxide with substituted anilines catalysed by **24a**, **24b**, **25a** and **25b**. Adapted from ref. ³⁵.

large SAVs of volume 1861 and $2637.5 \text{ \AA}^3$, corresponding to 29 and 20% of the cell volume, respectively. In contrast, CPs **25a** and **25b**, with *meta*-arylcarboxylate groups, offered negligible SAVs at 2.3 and 0.3% per unit cell, respectively. All four CPs functioned as heterogeneous and reusable catalysts for the regio-, stereo-, as well as chemo-selective ring-opening reactions of various epoxides. The cyanation reactions of assorted aldehydes, varying by their molecular sizes, were used to rationalize that the product transformation depended on the relative size match of pore size offered by CPs to that of molecular size of a substrate.

Gupta and co-workers³⁶ have further demonstrated the synthesis of CPs $[\text{Mn}_5(\mathbf{24})_2(\text{H}_2\text{O})_{11}]$ (**24c**), $[\text{Co}_3(\mathbf{24})(\mu\text{-OH})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_4]$ (**24d**), $[\text{Mn}_2(\mathbf{25})(\mu\text{-OH})(\text{H}_2\text{O})_3]$ (**25c**) and $[\text{Co}_2(\mathbf{25})(\mu\text{-OH})(\text{H}_2\text{O})_3]$ (**25d**) by the reaction of metalloligands **24** and **25** with $\text{Mn}(\text{OAc})_2$ and $\text{Co}(\text{OAc})_2$, respectively (Figure 16). In all four CPs, the appended groups were present in their completely deprotonated arylcarboxylate form and were involved in coordinating to the secondary metal ions to give 3D architectures. Notably, CPs **24c** and **24d** with *para*-arylcarboxylate groups, offered pores with larger cross sections of $19.96 \times 18.50 \text{ \AA}^2$ (for **24c**) and 11.15×7.46 and $11.83 \times 11.69 \text{ \AA}^2$ (for **24d**) whereas **25c** and **25d** with *meta*-arylcarboxylate fragments displayed smaller pores of $8.79 \times 8.34 \text{ \AA}^2$ and $8.06 \times 7.98 \text{ \AA}^2$ cross-section area, respectively. All four CPs acted as heterogeneous catalysts for the olefin epoxidation reactions using $t\text{BuOOH}$ as an oxidant under solvent- and additive-free conditions. These CPs

illustrated noteworthy structural stability and therefore good reusability.

Gupta and co-workers⁶² have further utilized metalloligand **24** to synthesize lanthanide-based CPs $[\text{Eu}(\mathbf{24})(\text{H}_2\text{O})_5]$ (**24e**) and $[\text{Tb}(\mathbf{24})(\text{H}_2\text{O})_5]$ (**24f**) (Figure 17). The nine-coordinated Eu^{3+} ion in **24e** exhibited two bidentate $\text{O}_{\text{carboxylate}}$ groups stemming from two different metalloligands whereas the remaining sites were occupied by water molecules. The octa-coordinated Tb^{3+} ion in **24f** had ligations by three $\text{O}_{\text{carboxylate}}$ atoms from two different metalloligands and five water molecules. In both cases, metalloligands are coordinated to the lanthanide ions and generated 1D chains. Several 1D chains are further connected to each other *via* an array of hydrogen bonds involving O_{amide} , $\text{O}_{\text{carboxylate}}$ and O_{COOH} groups together with coordinated and lattice water molecules. CPs **24e** and **24f** acted as the heterogeneous catalysts for the ring-opening reactions of assorted epoxides utilizing several nucleophiles under the solvent-free conditions.

The metalloligand **24** on reaction with $\text{Ni}(\text{OAc})_2$ produced an interesting CP $[\text{Ni}_2(\mathbf{24})(\text{H}_2\text{O})_8]$ (**24g**).⁶³ Herein, a metalloligand **24** offering four arylcarboxylate groups, coordinated four different Ni(II) ions in various directions generating a porous 3D chiral network. **24g** displayed hexagonal major ($25.98 \times 27.47 \text{ \AA}^2$) and triangular minor ($8.84 \times 9.75 \text{ \AA}^2$) pores throughout the network structure (Figure 17d). **24g** functioned as the reusable heterogeneous catalysts for the C–S cross-coupling reactions between substituted aromatic

Figure 16. (a) Synthetic route for CPs **24c**, **24d**, **25c** and **25d**. (b) Structure of **24c** showing coordination of metalloligand **24** with Mn^{2+} ions. (c) Structure of **24d** showing coordination of metalloligand **24** with Co^{2+} ions. (e) Structure of **25c** showing coordination of metalloligand **25** with Mn^{2+} ions. (e) Structure of **25d** showing coordination of metalloligand **25** with Co^{2+} ions. (f) Epoxidation of styrene using $t\text{-BuOOH}$ catalysed by **24c**, **24d**, **25c** and **25d**. Adapted from ref. ³⁶.

Figure 17. (a) The synthetic route for CPs **24e**, **24f** and **24g**. (b) Structure of **24e** showing coordination of metalloligand **24** with Eu^{3+} ions. (c) Structure of **24f** showing coordination of metalloligand **24** with Tb^{3+} ions. (d) Structure of **24g** showing coordination of metalloligand **24** with Ni^{2+} ions. (e) Ring-opening reactions of styrene oxide and cyclohexene oxide with aniline catalyzed by **24e** and **24f**. (f) C-S cross coupling reaction catalysed by **24g**. Adapted from ref. ⁶² and ⁶³.

Figure 18. (a) Synthetic route for CPs **26a**, **26b**, **27a** and **27b**. (b) Structure of **26a** showing coordination of metalloligand **26** with Zn^{2+} ions. (c) Structure of **26b** showing coordination of metalloligand **26** with Cd^{2+} ions. (d) Structure of **27a** showing coordination of metalloligand **27** with Zn^{2+} ions. (e) Structure of **27b** showing coordination of metalloligand **27** with Cd^{2+} ions. (f) Knoevenagel condensation of assorted aldehydes catalyzed by **26a**, **26b**, **27a** and **27b**. Adapted from ref. ⁶⁴.

halides and thiophenol as well as cyclohexanethiol and ethanethiol. The importance of earth-abundant nickel-based CP increased manifold as the catalytic reactions were successful both with aromatic and aliphatic sulphur-based nucleophiles while carrying out the reactions heterogeneously.

Utilizing two unique metalloligands **26** and **27** offering appended arylcarboxylic acid groups at the strategically placed positions, Gupta and co-workers⁶⁴ have developed following CPs: $[\text{Zn}_3(\text{26})(\text{H}_2\text{O})_5]$ (**26a**), $[\text{Cd}_4(\text{26})_2(\text{H}_2\text{O})_4]$ (**26b**), $[\text{Zn}_2(\text{27})_2\text{Na}_2(\text{H}_2\text{O})_{13}]$, (**27a**) and $[\text{Cd}(\text{27})(\text{H}_2\text{O})\text{Na}(\text{H}_2\text{O})_5]_n$ (**27b**) (Figure 18). All four CPs were found to offer significant SAVs suggesting considerable porosity of CPs. All four CPs displayed orderly arrangement of secondary metals and unique network topologies. These networks were shown to act as the heterogeneous and reusable catalysts for the Knoevenagel condensation reactions and cyanation reactions of assorted aldehydes. Importantly, cyanation reactions demonstrated the substrate size-exclusion catalysis wherein a correlation was noted between the pore sizes being offered by a CP to that of molecular size of a substrate.

Using an interesting metalloligand **28** offering eight arylcarboxylic acid groups, Gupta and co-workers³⁷ have reported three CPs: $[\text{Zn}_8(\text{28}')_2\text{Na}_2(\text{H}_2\text{O})_{21}]_n$ (**28a**), $[\text{Cd}_8(\text{28}')(\text{28}'')]$

$(\text{H}_2\text{O})_{21}]_n$ (**28b**), and $[\text{Mn}_8(\text{28}')_2\text{Na}_2(\text{H}_2\text{O})_{27}]$ (**28c**) (Figure 19). In these CPs, metalloligand **28** was found to coordinate secondary metals either through all eight carboxylate groups (**28'** form) or *via* six COO^- and two $-\text{COOH}$ groups (**28''** form). The crystal structure displayed 3D nature for all three CPs wherein metalloligands are connected through secondary metals. The molecular structures of these CPs were quite different and consisted of pores of varying dimensions. All three CPs acted as the heterogeneous catalysts for the Knoevenagel condensation reactions of assorted aldehydes. These catalysts could be recycled several times without significant loss of reactivity suggesting their robust nature.

2.4 Coordination polymers based on bipyridine-based metalloligands

Bipyridines (2,2', 3,3' and 4,4'-bipyridine) are some of the highly utilized ligands in coordination and supramolecular chemistry.^{65–67} The major interest with bipyridine and related ligands are due to their rich photo-physical properties and noteworthy redox features that have been frequently utilized in assorted research fields.^{67,68} Such ligands have also found

Figure 19. (a) Synthetic route for CPs **28a**, **28b** and **28c**. (b) Structure of **28a** showing coordination of metalloligand **28** with Zn^{2+} ions. (c) Structure of **28b** showing coordination of metalloligand **28** with Cd^{2+} ions. (d) Structure of **28c** showing coordination of metalloligand **28** with Mn^{2+} ions. (e) Knoevenagel condensations of assorted aldehydes with ethyl cyanoacetate, 1,3-cyclohexanedione and malononitrile catalyzed by **28a–28c**. Adapted from ref. ³⁷.

applications for the construction of designer materials as well as for the synthesis of metalloligands.⁶⁹

Lin and co-workers⁷⁰ have synthesized a highly porous and phosphorescent Ir-containing CP $[\text{Zn}_4(\mathbf{29})_2(\mu^4\text{-O})](\mathbf{29a})$ where three carboxylate groups from three bipyridine-based metalloligands **29** coordinate to four Zn(II) ions to form $[\text{Zn}_4(\mu^4\text{-O})(\text{OOCR})_6]$ SBUs (Figure 20). A combination of SBUs and metalloligands generated 2D bilayers that exhibited channels of dimensions $7.9 \times 4.3 \text{ \AA}^2$ containing guest solvent molecules. N_2 adsorption at 77 K and CO_2 adsorption at 273 K showed permanent porosity in **29a** indicating its microporous architecture with N_2 BET surface area of $764 \text{ m}^2/\text{g}$. Thin coating of desolvated **29a** was created on the surface of a KBr pellet that showed emission at 538 nm. Such a composite demonstrated efficient oxygen sensing *via* reversible luminescence quenching at 1 atm. pressure of O_2 .

Luo and co-workers⁷¹ have synthesized an In-based highly symmetrical CP $[\text{In}(\mathbf{30})_3(\text{CH}_3)_2\text{NH}_2](\mathbf{30a})$ utilising

Ru-bipyridine-based metalloligand **30** (Figure 21). **30a** displayed 3D open channels throughout the network structure and solvent accessible volume of ca. 70%. **30a** exhibited broad visible light absorption and strong red light emission with long decay lifetime, both of which originated from metal-to-ligand charge transfer within the metalloligands. Due to notable light harvesting and redox nature of metalloligand in **30a**, its photocatalytic activities were illustrated by visible light induced photo-degradation of methyl orange. Results indicated that **30a** was a stable and remarkable visible-light driven heterogeneous photocatalyst. Electron-rich **30a** also illustrated selective detection of electron-deficient nitro explosive molecules.

Luo and co-workers⁷² have utilized metalloligand **31** to synthesize a Cd(II)-based CP $[\text{Cd}(\mathbf{31})(\text{H}_2\text{O})_3](\mathbf{31a})$ (Figure 22). This CP exhibited large 3D void space which readily allowed a second framework *via* interpenetration leading to a two-fold interpenetrating architecture. The solid-state UV-Vis

Figure 20. Synthetic route and structure of CP **29a** showing coordination of metalloligand **29** with Zn^{2+} ions; adapted from ref. ⁷⁰.

Figure 21. Synthetic route and composition of CP **30a**; adapted from ref. ⁷¹.

spectrum displayed broad absorption bands between 400 and 650 nm which were assigned to metal-to-ligand charge transfer transitions based on Ru-metalloligand. The photocatalytic potential of **31a** was evaluated by investigating its photochemical activities for the reduction of CO_2 producing HCOO^- under visible-light irradiation. **31a** produced 17.2 μmol of HCOO^- in 6 h with 0.54% quantum yield. This was an interesting example where the stability of a photocatalyst was improved as a result of network interpenetration.

2.5 Coordination polymers based on miscellaneous metalloligands

In addition to the aforementioned classes of metalloligands, this section discusses a few other miscellaneous metalloligands offering carboxylic acid groups that are originated from different platforms.

Huang and co-workers⁷³ have illustrated a novel step-wise strategy for the construction of heterometallic CPs $[\text{Cu}(\mathbf{32})(\text{bipyridine})_3(\text{H}_2\text{O})_5]$ (**32a**) and $\{[\text{Zn}_3(\mathbf{32})(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3(\text{H}_2\text{O})_4]\}$ (**32b**) based on a hexanuclear $\text{Ag}(\text{I})$ -based metalloligand **32** (Figure 23). In **32a**, partial participation of carboxylate groups in coordination to the $\text{Cu}(\text{II})$ ions was due to the combined reasons of steric hindrance and charge neutrality whereas bipyridine compensated the additional coordinations. As a result, the polymer grew in only

one direction generating 1D chain. In contrast, **32b** displayed full participation of carboxylate groups in coordination to $\text{Zn}(\text{II})$ ions producing a 2D sheet architecture where ethylenediamine (eda) also acted as a bridging ligand. Interestingly, $\text{Zn}(\text{II})$ ions exhibited both octahedral and tetrahedral coordination geometries in this CP.

Absorption spectra of **32a** and **32b** were measured in the solid state at room temperature. In both cases, intense absorption bands in the range of 200–500 nm were assigned to be based on metalloligands. In **32a**, a low energy band was noticed at ca. 630 nm due to metal-centred transition. **32b** showed blue-shifted photoluminescence at 515 nm suggesting that the energy level of LMCT excited state of metalloligand was changed due to the incorporation of $\text{Zn}(\text{II})$ centres. These examples illustrated that the introduction of SBUs significantly influenced the photoluminescence behaviour of metalloligands.

Using metalloligand **33**, Su and co-workers⁷⁴ have synthesized a 2D CP $[\text{Eu}(\mathbf{33})(\text{H}_2\text{O})(\text{DMA})](\mathbf{33a})$ under the solvothermal conditions (Figure 24). The crystal structure exhibited that the CP was constituted of $[\text{Eu}_2(\text{OOCR})_6(\text{DMA})_2(\text{H}_2\text{O})_2]$ SBUs in which nine-coordinated Eu atoms received seven coordinations from $\text{O}_{\text{carboxylate}}$ groups and two each from DMA and water molecules. The florescent measurements, which allowed fine-tuned luminescence properties, yielded narrow and characteristic peaks due to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions of the $\text{Eu}(\text{III})$ ion when excited at 396 nm. The solvent-dependent luminescent behaviour of **33a** suggested potential application that was confirmed by showing the detection of nitrobenzene in the form of fluorescence quenching. Further, **33a** displayed anti-interference ability and could be used for sensing in complicated component system.

Su and co-workers⁷⁵ reported a new family of heterometallic CPs $[\text{Eu}(\mathbf{34})(\text{NO}_3)]$ (**34a**), $[\text{Tb}(\mathbf{34})(\text{NO}_3)]$ (**34b**), $[\text{La}_2(\mathbf{34})(\text{NO}_3)_3(\text{DMA})]$ (**34c**) based on metalloligand **34** (Figure 25). The Ln metal ions coordinated to the carboxylate groups originated from metalloligand **34** resulting into heterometallic architectures. These CPs exhibited high luminescence quantum yield, narrow band width, long lived

Figure 22. Synthetic route and structure of CP **31a** showing coordination of metalloligand **31** with Cd^{2+} ions; adapted from ref. ⁷².

Figure 23. (a) Synthetic route for CPs **32a** and **32b**. (b) Structure of **32a** showing coordination of metalloligand **32** with Cu^{2+} ions. (c) Structure of **32b** showing coordination of metalloligand **32** with Zn^{2+} ions. Adapted from ref. ⁷³.

emission and large Stokes shift. In **34a**, two Eu^{3+} ions coordinated to eight carboxylate groups from six different metalloligands forming $[\text{Eu}_2(\text{CO}_2)_8]$ SBUs. Such SBUs were connected to metalloligands generating 3D framework having large pores of $19.30 \times 23.79 \text{ \AA}^2$ dimensions. In this CP, metalloligand **34** and $[\text{Eu}_2(\text{OOCR})_8]$ SBUs acted as 3- and 6-connected nodes, respectively. The crystallographic studies revealed that **34b** was isostructural to **34a**. In **34c**, La atoms were linked by carboxylate groups and NO_3^-

to form tetranuclear $[\text{La}_4(\text{OOCR})_8(\text{NO}_3)_6(\text{DMA})_2]$ SBUs. These SBUs were connected to metalloligands giving rise to a 3D framework with pores of $3.72 \times 13.64 \text{ \AA}^2$. On excitation at 253 nm, **34a** exhibited an intense red luminescence due to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions. Tb-based **34b**, when excited at 291 nm, exhibited typical emission bands at 489, 545, 584, and 621 nm. For **34a**, decay profile of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 616 nm was biexponential yielding lifetime 11.04 μs whereas for **34b**, decay profile provided the lifetime value of 6.53 μs .

Figure 24. Synthetic route and structure of CP **33a** showing the coordination of **33** with Eu^{3+} ions; adapted from ref. ⁷⁴.

Figure 25. (a) Synthetic route for CPs **34a–34c**. (b) Structure of **34a** and **34b** showing coordination of metalloligand **34** with Eu^{3+} and Tb^{3+} ions, respectively. (c) Structure of **34c** showing coordination of metalloligand **34** with La^{3+} ions. Adapted from ref. ⁷⁵.

Humphrey and co-workers⁷⁶ have used a $\text{Pd}(\text{II})$ -PCP complex as an interesting metalloligand for the synthesis of cobalt-based CP with notable chemical reactivity (Figure 26). The air- and moisture-stable metalloligand **35** acted as a rigid tetratopic linker for the synthesis of robust $\text{Co}(\text{II})$ -based CP **35a**. The crystal structure of **35a** exhibited the presence of $\text{Pd}-\text{Cl}$ groups inside the pores that were accessible for the post-synthetic modifications that facilitated chemical reactions previously unobserved. A post-synthesized CP having

$\text{Pd}-\text{CH}_3$ species underwent rapid CO_2 insertion to give $\text{Pd}-\text{OC}(\text{O})\text{CH}_3$. Importantly, while $\text{Pd}-\text{CH}_3$ based CP was highly selective for the adsorption of CO_2 over CO ; a $\text{Pd}-\text{N}_3$ based CP resisted CO_2 insertion under the identical reaction conditions.

Trikalitis and co-workers⁷⁷ have reported a $\text{Pd}-\text{Cu}$ -based CP **36a** utilizing a simple metalloligand **36**. Such metalloligands were linked to the $\text{Cu}(\text{II})$ ions through paddlewheel $[\text{Cu}_2(\text{OOCR})_4]$ SBUs (Figure 27). The crystal structure of

Figure 26. Synthetic route and structure of CP **35a** showing coordination of metalloligand **35** with Co^{2+} ions; adapted from ref. ⁷⁶.

Figure 27. Synthetic route and structure of CP **36a** showing coordination of metalloligand **36** with Cu^{2+} ions; adapted from ref. ⁷⁷.

36a displayed two types of cavities made up of either 12 metalloligands and 6 paddlewheel SBUs or made up of 6 metalloligands and 12 paddlewheel SBUs with an internal diameter of 10 Å. The total solvent accessible volume was found to be 64%. Argon adsorption isotherm at 87 K confirmed the permanent porosity of **36a** by showing fully reversible type-I isotherm, characteristic of a microporous material. The BET and Langmuir surface area were found to be 1568 and 1654 $\text{m}^2 \text{g}^{-1}$, respectively. The total pore volume, calculated from argon adsorption isotherm at 0.999 p/p_0 was 0.60 $\text{cm}^3 \text{g}^{-1}$, suggesting that the structure remained fully intact after activation. A remarkable CO_2 uptake was observed reaching ca. 201 $\text{cm}^3 \text{g}^{-1}$ (ca. 40 wt%) and ca. 125 $\text{cm}^3 \text{g}^{-1}$ (20 wt%) at 273 and 298 K, respectively, at 1 bar. These values illustrated remarkably high sorption characteristics in the family of framework materials.

Boomishankar and co-workers⁷⁸ have demonstrated an interesting transformation of a cubic cage $[(\text{Pd}_3(\text{X})_8(\text{Y})_{12})]$ ($\text{X} = \text{PO}(\text{NiPr})_3$ and $\text{Y} = 2,5\text{-pyrazenedicarboxylate}$) **37** into a 3D framework (**37a**). Treatment of $[\text{Pd}_3\text{X}]^{3+}$ with 2,5-pyrazenedicarboxylic acid (Y) yielded a cubic cage metalloligand **37**. Metalloligand **37** is comprised of eight

$[\text{Pd}_3\text{X}]^{3+}$ units at the vertices and twelve bridging 2,5-pyrazenedicarboxylate anions forming the edges. The reaction of **37** with $\text{Zn}(\text{NO}_3)_2$ in MeOH yielded $[\text{Zn}_2(\text{Pd}_3\text{X})_4(\text{Y})_6(\text{H}_2\text{O})_4]$ (**37a**) consisting of a 3D network where coordination sphere of $\text{Zn}(\text{II})$ ions exhibited an 8-coordinate square-antiprismatic environment. The basic structural motif in **37a** consists of Pd_3X -based tetrahedral nodes that are connected through secondary Zn^{2+} ions. The cage– Zn –cage angle of 145° provides a close packing of cages enabling van der Waals interactions between the cages (Figure 28).

3. Concluding remarks and future outlook

This review has highlighted various metalloligands offering appended carboxylic acid groups in the design and the synthesis of coordination polymers (CPs). The examples presented herein not only illustrated the importance of appended carboxylic acid groups in dictating the coordination properties of a metalloligand but also in controlling the dimensionality of

Figure 28. Synthetic route and structure of CP **37a** showing coordination of metalloligand **37** with Zn^{2+} ions; adapted from ref. ⁷⁸.

the resultant CPs. These examples also demonstrated the significance of metalloligands in the development of functional materials where the functional properties (or application) are often related to the selection of a metalloligand. Examples included highly porous CPs for gas sorption and storage properties, porous CPs as the luminescent materials, porous CPs as the sensors; and porous and stable CPs as the heterogeneous catalysts. It is believed that these examples of metalloligands offering carboxylic acid groups will stimulate the development of next-generation metalloligands with improved design aspects, better photophysical properties, and enhanced stability towards noteworthy coordination polymers with fascinating structural features and notable functional properties and applications.

Notes

In order to maintain focus on the architectures of coordination polymers (CPs), lattice solvent molecules have been omitted both from the compositions and structures of the resultant CPs.

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