Highly stable olefin–Cu(I) coordination oligomers and polymers

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Highly stable Cu(I)–olefin coordination oligomers and polymers have been successfully prepared and applied to construct metal–organic frameworks (MOFs) with interesting physical and chemical functions in recent years. In this review, we present the olefin–Cu(I) coordination oligomers and polymers and their novel physical properties. From structure to functions, particular emphasis is placed on the coordination and organometallic chemistry of olefin–Cu(I) coordination oligomers and polymers, their structures and potential applications as solids possessing unusual physical functional properties such as electrochemical, chiral separation, fluorescent sensing and ferroelectricity.

1 Introduction

In recent years, molecular architecture and self-assembly of coordination polymers has attracted much attention in coordination and organometallics chemistry.[1] Among the transition metals, copper(I) has played a central role in the construction of supramolecular array supports by a variety of nitrogen, oxygen, sulfur and phosphorus donor ligands.[1] However, in contrast to the many examples of coordination polymers based on self-assembly of Cu(I) ion and organic ligands that have been studied, there are only a handful of reports on the chemistry of supramolecular compounds containing olefin as building block are little concerned.

Olefin–copper(I) complexes are known to play an important role in biochemistry and modern organic chemistry and are employed as active species in copper catalysis. At the beginning of 20th century, it was shown that olefins react with cuprous salts in solution or solid state. Manchot and Brandt found that ethylene and cuprous chloride reacted to form an unstable compound which may be regarded as the first olefin–Cu(I) complex.[2a] Since its discovery, a myriad of olefin–Cu(I) complexes have been studied. However, their structures were unknown until a report on the cuprous chloride complex, 1,5-cyclocatadine (COD) by van den Hende and Baird in 1963.[2b] The pioneering work of Thompson and co-workers demonstrated the first stable Cu(I)–olefin complexes in 1983.[2c] In the following years the area experienced rapid development, and this has led to the synthesis and structural characterization of a large number of Cu(I)–olefin coordination oligomers and polymers. Recently, this novel strategy of highly stable Cu(I)–olefin self-assembly has been successfully applied to construct metal–organic frameworks (MOFs) with interesting physical and chemical functions.

Although several excellent review articles on coordination supramolecular chemistry have also included some aspects of Cu(I)–olefin,[3] there appears to be no review article that deals exclusively with this class of Cu(I)–olefin structures, and

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focuses on their functional properties. Significant progress has been made in the past few years in the area of functional Cu(I)–olefin assemblies. In this review, we highlight the recent advances in highly stable Cu(I)–olefin coordination oligomers and polymers and discuss their potential applications as solids possessing unusual physical functional properties.

2. Structural motifs

Since 1996, investigations on Cu(I)–olefin coordination polymers have significantly intensified, and much attention has been devoted to the construction of interesting supramolecular architectures. Considering exclusively the Cu(I)–olefin interactions, a variety of structural motifs have been observed for these molecular architectures, including four groups oligomers, chain (including ribbon), layered and network structures. In general, halogen atoms (Cl, Br) act in a bridging coordination mode, such as μ_2-, or μ_3- bridging modes to Cu(I) in the entire Cu(I)–olefin coordination polymers, which is in contrast to those found in other metal complexes of olefin. Here they can be seen as spacers in one-dimensional chains or as nodes in the two-dimensional nets. Usually, the coordination number of Cu (I) in Cu(I)–olefin coordination polymers is 3–4, spanning the T-shaped (or Y-shaped) and tetrahedral geometries with all the coordination modes η^2 type. In this section, we concentrate on coordination modes, the construction of olefin–Cu(I) oligomers and one-, two-, three-dimensional and homochiral polymers.

2.1 Coordination mode

The nature of coordination between the Cu(I) and olefin can be generally described by the Dewar–Chatt–Duncanson model[4] which includes both σ and π contributions as shown in Fig. 1. The π-bond consists of two components: the (Cu(I) $\leftarrow$ L), donor–acceptor component arising from overlapping of the occupied olefin π p orbital and the unoccupied $4s^0$ orbital of the Cu(I) atom which is the dominant in the bond, and the (Cu(I) $\rightarrow$ L) p-dative component, which is formed upon electron-density drawing-off from the $3d^{10}$ Cu(I) orbitals to the unoccupied antibonding orbital of the C=C-group. Thus, an effective metal – (C=C) p-interaction is required to reveal both of them.

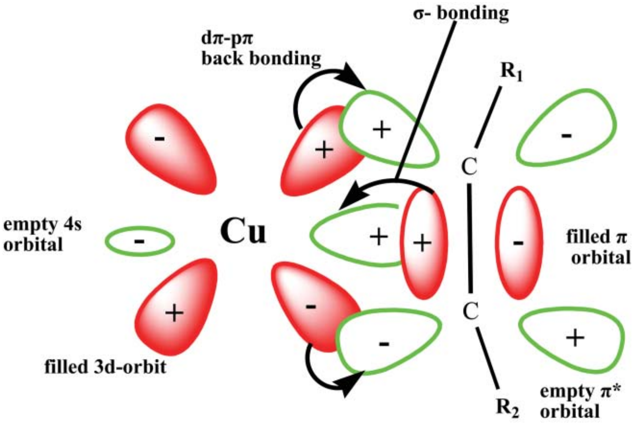
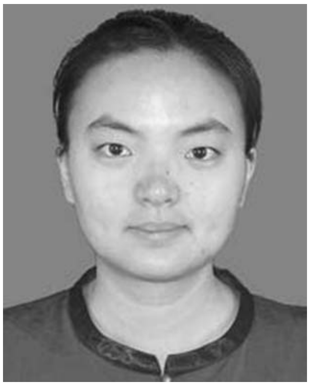


Fig. 1 A qualitative orbital description of copper–alkene bonding

2.2. Oligomers motifs

There are three types of olefin–Cu(I) coordination oligomers which are divided by the connecting node, such as dimer, eight-membered ring and finite chain.

[(n-H_2PYA)$_2Cu_2Cl_4$] (**1**(n = 2), **2**(n = 3), **3**(n = 4))[5] (HPYA = pyridyl acrylic acid) features a dimeric Cu(I)–olefin complex (Fig. 2), in which the Cu(I) ion is coordinated in a distorted tetrahedral geometry defined by two bridging μ_2-Cl ligands, one terminal Cl^- ligand, and the C=C moiety in 2-H_2PYA. Interestingly, the pyridyl group is protonated to which prevents coordination, and the carboxylate groups are



Hong Zhao

Hong Zhao was born in 1976 in Jiangsu, P. R. China. She graduated in Chemistry in 1999 at Xuzhou Normal University where she also received her Master's Degree. From 2002 she studied in the group of Prof. Xiong and received her PhD in 2004. Her research interests are concentrated on chiral ligand synthesis, explorations of the homochiral functional coordination polymers and triboluminescent compounds. She is presently a postdoc in the Chemistry Department at the University of Puerto Rico. She is an author in more than ten scientific publications and review articles. She was awarded a GE Foundation Scholarship of Nanjing University in 2004.

Ren-Gen Xiong

Ren-Gen Xiong was born in 1961 in Jiangxi, P. R. China, and obtained his degrees of BSc (1982), MSc (1987) and PhD (1994) at the University of Logistical Engineering. He then pursued work, first at the Coordination Chemistry Institute at Nanjing University (1994–1996), then at the Department of Chemistry at Puerto Rico University (1996–1997) and finally at the Chemistry Department, Brandeis University (1997–1998). In 1999, he was a visiting scholar at the Chemistry Department at Boston College. Later that same year, Prof. Xiong returned to China to take up a Professorship at the University of Nanjing. His research interests include chiral ligand synthesis and enantioseparation, homochiral functional zeolite-analogues, olefin–copper chemistry and triboluminescence. He is the author of more than 100 scientific publications, review articles, and a book. He has been honored with the first Zhong-Cheng-Xin Award from the Chemistry Department of NJU and the second-class Award of National Science in China (name rank 2).

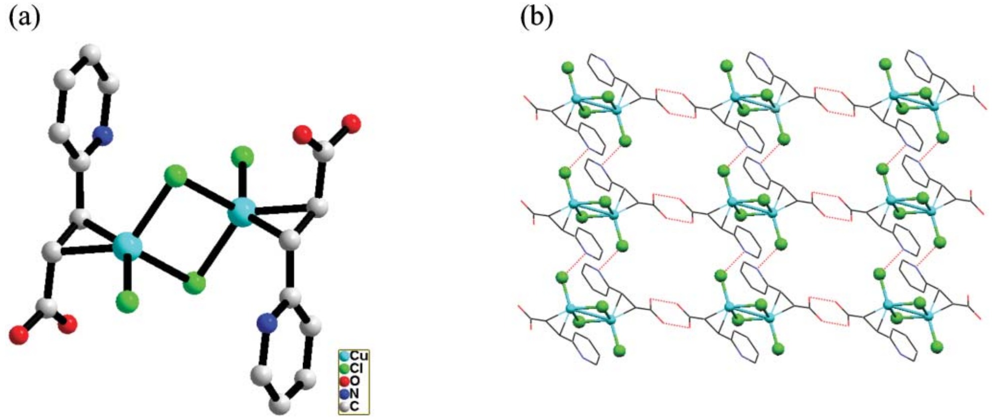


Fig. 2 (a) The crystal structure of **1**. (b) 3-D network representation of **1** though H-bonds. (Red dotted lines stand for H bondings, H atoms are omitted for clarity.)

uncoordinated as well. The carboxylate groups are H-bonded with other $(2\text{-}H_2PYA)_2Cu_2Cl_4$ units. Strong H-bonds between protonated N atom and terminal Cl ligands were also observed. These strong H-bond interactions and π–π stacking give a highly stable 3-D network (Fig. 2b). Figure 3 represents the dimeric structures of **2** and **3**. They also display H-bonding and π–π stacking interactions that result in the formation of 3D network similar to that found in **1**. Clearly, the three compounds formed are highly thermally stable, as the TGA of their polycrystalline showed no weight loss below *ca*. 232, 183, and 168 °C, respectively.

$[Cu_4Br_4(N\text{-allyl-2-furylaldimine})]$ (**4**) has a unique Cu_4Br_4 eight-membered ring Cu(I)–olefin complex (Fig. 4a),[6] which involves separate π and σ -coordinations of copper(I) in the form of planar trigonal geometry defined by two bridging μ_2-Br ligands, and the C=C moiety or N atoms in

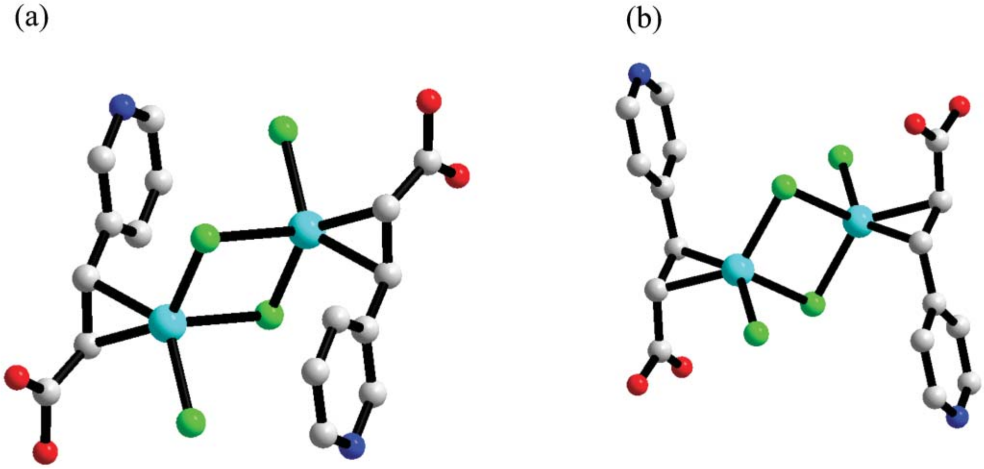


Fig. 3 (a) and (b) The dimeric structures of **2** and **3** in which their 3D networks also formed through H-bonding (such as N–H···Cl), similar to that found in **1**.

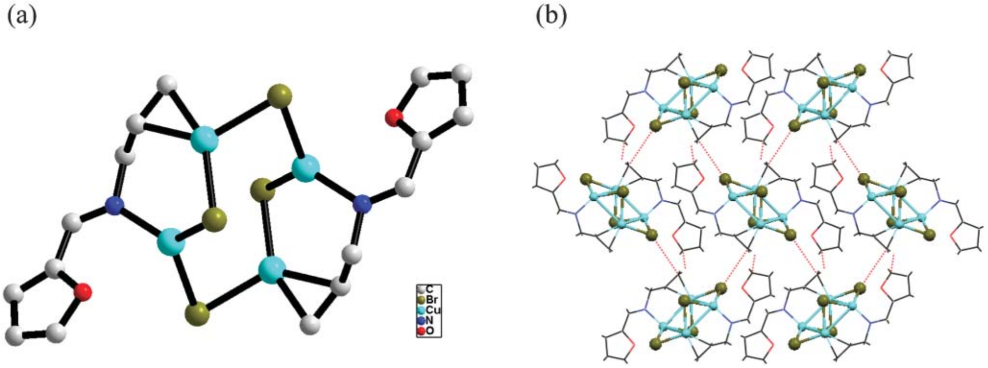


Fig. 4 (a) The crystal structure of **4**. (b) 3-D network representation of **4** though H-bonds.

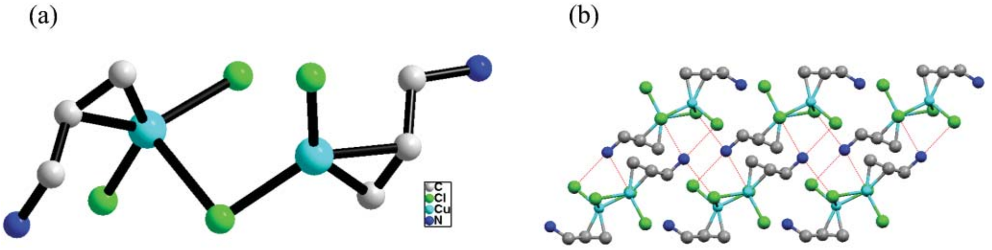


Fig. 5 (a) The crystal structure of **5**. (b) 3-D network perspective view of **5** though H-bonds.

the *N*-allyl-2-furylaldimine ligand. Four Cu atoms and Br atoms alternate to form an eight-membered ring. It is interesting to note that strong H-bond interactions also give rise to the formation of a stable 3-D network (Fig. 4b).

[Cu_2Cl_4(allylammonium)] (**5**) displays a monomeric finite chain Cu(I)–olefin complex (Fig. 5),[7] whereby the Cu(I) ion is coordinated in a distorted planar trigonal geometry defined by two bridging μ_2-Cl ligands, one terminal Cl^- ligand, and the C=C moiety in allylammonium. Interestingly, the amino group is protonated and H-bonded to other [Cu_2Cl_4(allylammonium)] units. Thus, strong H-bonds found between the protonated N atom and terminal Cl ligands result in the formation of a highly stable 3-D network through H-bond interactions (Fig. 5b)

It can be seen from the above-mentioned examples that strong H-bond and π–π stacking interactions may be responsible for their highly thermal stability, similar to weak H-bonds in organic solids capable of stabilizing the secondary structure of biomolecules such as DNA.

2.3 One-dimensional supramolecular motifs

Taking only the topological structure of 1D olefin–Cu(I) into consideration, there are three types of 1D structural supramolecular motifs that are extended by single- and double-chains and ribbons.

{[(2,2′-bpy)(4-HPYA)Cu(I)](BF_4)}$_n$, (2,2′-bpy = 2,2′-bipyridine) (**6**) was obtained by the treatment of 4-HPYA, 2,2′-bpy and Cu(MeCN)$_4$(BF_4) under solvothermal reaction conditions.[8] In the structure of **6**, the Cu(I) ion is coordinated in a distorted tetrahedral geometry and the ligand 4-HPYA acts as a neutral bidentate spacer links the two Cu(I) ions with a N atom and an olefin moiety (Fig. 6a) to give rise to a novel 1D straight line chain coordination polymer (Fig. 6b). It is worthy noting that the H atom of the carboxylic acid of 4-HPYA is hydrogen-bonded to one of the fluorine atoms of BF_4^-, while the other three fluorine atoms of BF_4^- are also weakly hydrogen-bonded to the H atoms of the pyridine ring. Similarly, the carbonyl oxygen is hydrogen-bonded to the H atoms of the pyridine ring. In a similar manner found in oligomers-, there also are aromatic ring π–π interactions. {[(2,2′-bpy)(3-HPYA)Cu(I)](BF_4)}$_n$ (**7**)[9] possesses a novel 1D straight line chain (Fig. 7) which is similar to compound **6**.

{[(1,10′-phen)(4-HPYA)Cu(I)](BF_4)}$_n$ (1,10′-phen = 1,10′-phenathroline) (**8**) was obtained by reacting 4-HPYA and 1,10-phenanthroline with Cu(MeCN)$_4$(BF_4) under solvothermal reaction conditions (Fig. 8a).[9] As shown in Fig. 8b,

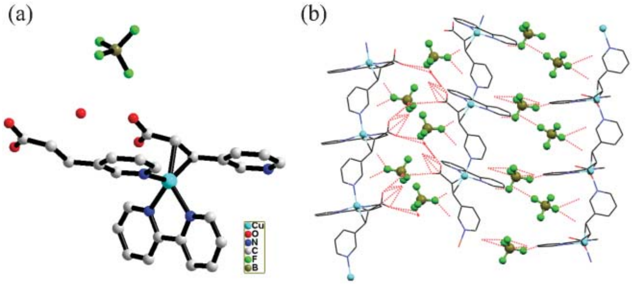


Fig. 7 (a) An asymmetry unit of compound **7**. (b) 3-D network perspective view of **7** though H-bonds.

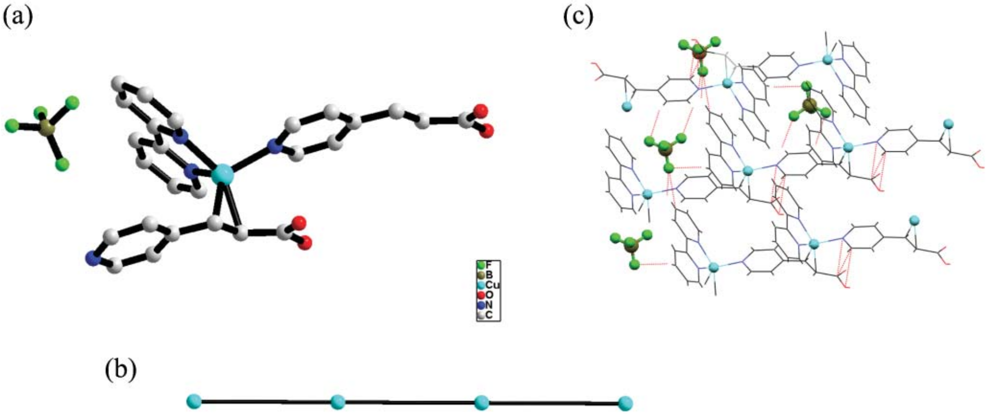


Fig. 6 (a) An asymmetry unit of compound **6**. (b) 3-D network perspective view of **6** though H-bonds. (c) Simplified 1D straight-line chain representation of **6**. The long straight line stands for 4-HPYA.

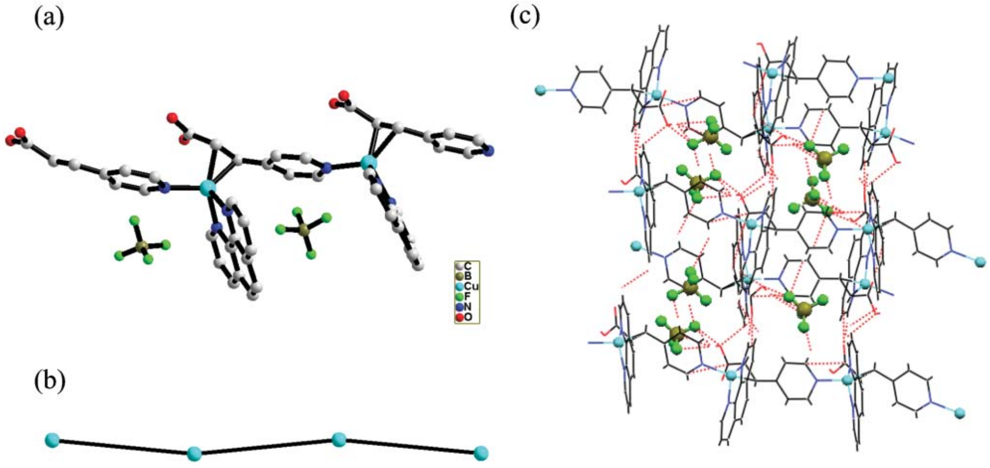


Fig. 8 (a) An asymmetry unit of compound **8**. (b) 3-D network perspective view of **8** though H-bonds. (c) Simplified 1D straight-line chain representation of **8**. The long straight line stands for 4-HPYA.

a new single zigzag chain with alternating Cu atoms and ligands is also found. Compounds **6**, **7** and **8** have highly thermal stability, probably due to the existence of strong hydrogen bonds and π–π stacking interactions of neighboring strands, thus resulting in the formation of stable 3D networks (Fig. 6c, Fig. 7b & Fig. 8c).

The coordination polymer [Cu_2Br_2(hex-5-en-2-one azine)] (**9**) is also a 1D infinite single zigzag chain with Cu atoms, Cl atoms and olefin ligands (Fig. 9).[10]

[$Cu_4Br_4(TTT)_2]_n$ (**10**) (TTT = triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione) was prepared by reacting TTT with CuBr in methanol at 50–70 °C under solvothermal conditions.[11] In this complex, Cu_4Br_4 clusters are linked by TTT ligands to form a new one-dimensional double chain. The Cu and Br atoms occupy corners of a distorted cube and there are only 10 Cu–Br bonds in each cluster resulting in an open-cubane arrangement. The open-cubane unit has two unique Cu^I atoms each being coordinated by an olefin moiety and two bromide ions in approximately the same plane with the plane of the metal center (Fig. 10a). One of the Cu atoms is coordinated to an extra bromide ion located within the cubane unit. The third Cu–Br bond is almost perpendicular to the plane of the other donor atoms. Only two of the three arms of the TTT ligand are involved in coordination to the cubane units. The terminal carbon atom of the third arm is disordered over two sites. Double ligand bridges linking neighboring cubane units form a one-dimensional double chain (Fig. 10b).

[Cu_2Br_3(1,3-Diallylbenzotriazolium)] (**11**) was obtained from the reaction of $CuBr_2$ and an alcoholic solution of 1,3-diallylbenzotriazolium bromide under *AC* electrochemical conditions.[12] In the structure, the separate Cu_2Br_2 dimers are bridged by the bromine atom to form infinite double-chains. The ligand is coordinated to two metal atoms of different inorganic chains through the C=C bonds of both allyl groups. The two ligands and four Cu(I) atoms along with the two Br atoms form a six-membered ring which share one Cu atom with an adjacent dimer, resulting in a new 1D ribbon. The environment of each of the two crystallographically independent copper atoms comprises of three bromine atoms and the C=C moiety (Fig. 11).

Compound [Cu_3Cl_4(ADBA)] (**12**) was also prepared by *AC* electrochemical synthesis from *N*-allyl-4-(*N*′,*N*′-dimethylamino)benzaldimine (ADBA) and an ethanolic solution of $CuCl_2·2H_2O$ in the presence of carbamide.[13] The coordination polyhedron of the Cu atoms is trigonal pyramid with the planar triangle formed by the Cl atoms or the C=C double bond moiety. The structure is built

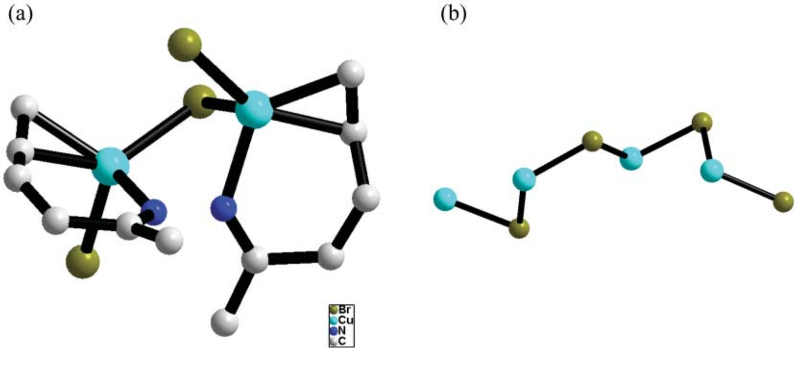


Fig. 9 (a) An asymmetry unit of compound **9**. (b) Simplified 1D zigzag chain representation of **9**. The long straight line stands for hex-5-en-2-one azine.

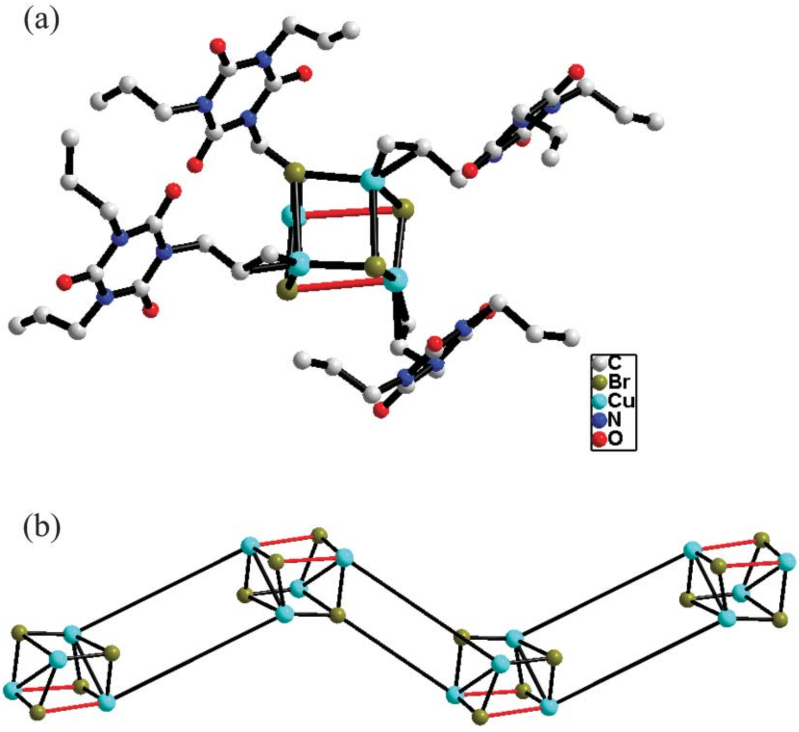


Fig. 10 (a) An asymmetry unit of compound **10**. (b) Simplified 1D double chain representation of **10**. The long straight line stands for TTT and the red lines stand for pseudo-linking line.

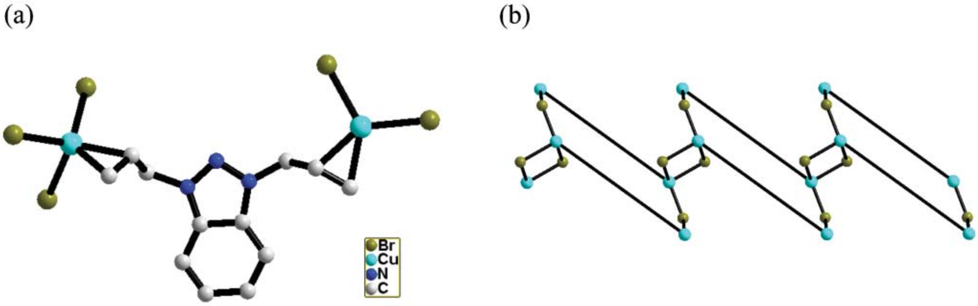


Fig. 11 (a) An asymmetry unit of compound **11**. (b) Simplified 1D ribbon representation of **11**. The long straight line stands for 1,3-diallylbenzotriazolium.

from the $[Cu_3Cl_4]_n^{n-}$ chains π-coordinated to the H^+ADBA cations. Compound **12** features one Cu_2Br_2 dimer adjoined to two irregular hexagonals, which share one Cu atom and Br atom, forming a distorted twelve-membered ring linked by two Cl atoms that results in the formation of 1D infinite ribbon (Fig. 12).

In summary, whether the connecting node is a dimer or a pseudo-cubane cluster, halo bridging plays a crucial role in the formation of 1-D infinite chains. In the absence of halo elements, auxiliary linking coordination atoms such as N are essentially needed, as evidenced in compounds **6**, **7** and **8**.

2.4 Two-dimensional supramolecular motifs

Eight structural units on two-dimensional olefin–copper (I) coordination polymers have been so far reported. Among these units, most describe multinuclear Cu(I) halide as the connecting node in networks on dimeric, *n*-membered ring, prismane and other complicated clusters with the carboxylate group acting as the bridging linker.

Complex $[Cu_6Br_6(TTT)_2]_n$ (**13**) was prepared by reacting TTT with CuBr in ethanol at 90 °C.[11] The solid-state structure indicates the presence of Cu_6Br_6 prismane clusters. Each Cu atom of the cluster is coordinated to three Br atoms and an olefin moiety. Each cluster is attached to six TTT ligands, each of which is attached to three prismane clusters. The resulting coordination polymer is a 2D framework with Cu_6Br_6 prismane clusters as connecting node (Fig. 13). It is interesting to note that complex **13** can be furnished from the reaction of complex **10** with CuBr in ethanol at 80–90 °C (Scheme 1).

$[Cu(3\text{-PYA})]_n$ (**14**) possesses a 2D infinite double-layered square framework. In the structure,[14] the Cu(I) ions are coordinated in a distorted tetrahedral geometry, 3-PYA acts as an anionic tetradentate spacer that links the four Cu(I) ions by using two carboxylate oxygen atoms, one N atom of the

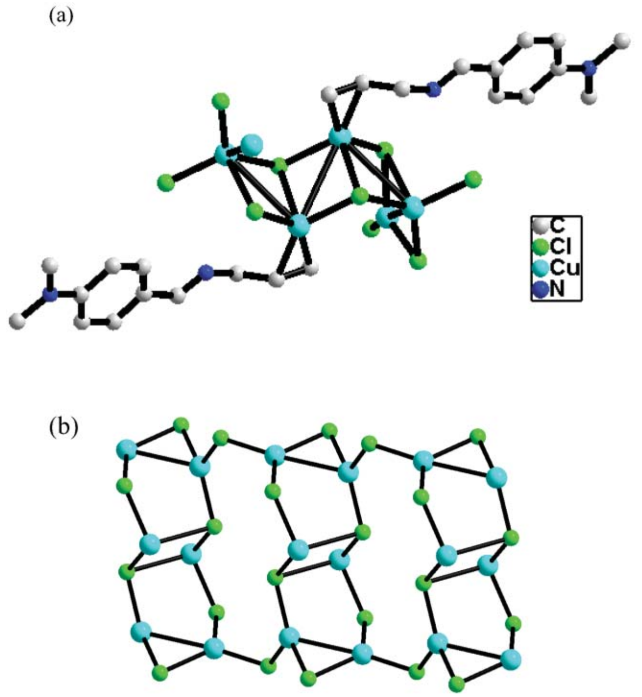
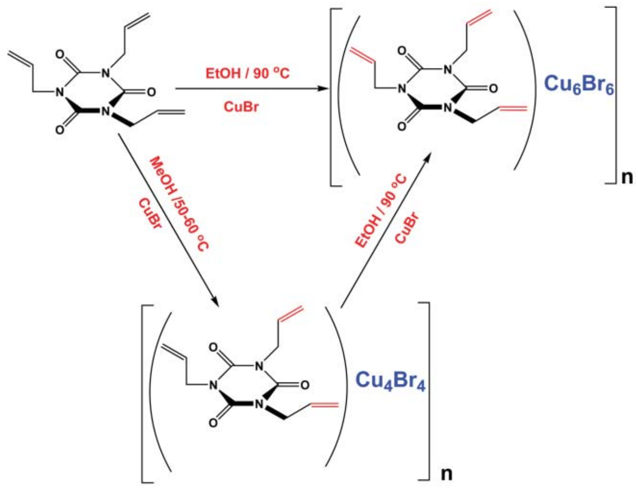


Fig. 12 (a) An asymmetry unit of compound **12**. (b) Simplified 1D ribbon representation of **12**.

pyridyl ring, and the olefin moiety to give rise to a novel 2D coordination polymer. Each carboxylate group adopts a *syn–syn* bidentate bridging mode that links two Cu atoms to form a chair-type eight-membered ring. There are weak stabilizing π–π interactions between adjacent two pyridyl rings, probably suggesting that π–π stacking of neighboring strands plays an important role in stabilizing compound **14** since it has a high decomposition temperature of about 265 °C (Fig. 14).

[(2-PYA)]$_n$ (**15**) was prepared under solvothermal reaction conditions by the reactions of $Cu(MeCN)_4(BF_4)$ with 2-HPYA in the presence of PPh_3.[14] Cu(I) ions in **15** are coordinated in a distorted tetrahedral geometry. Thus, 2-PYA acts as an anion tetradentate spacer to link four Cu(I) ions by using two carboxylate oxygen atoms, one N atom of the pyridyl ring, and the olefin moiety to give rise to a 2D coordination polymer. Each carboxylate group in **15** adopts a *syn–syn* bidentate bridging mode to link two Cu atoms to form three chair-type eight-membered rings. Similarly, there are many weak stabilizing π–π interactions (3.427 Å for **15**) of adjacent two pyridyl rings, suggesting that π–π stacking of neighboring strands plays an important role in stabilizing the compound **15** since its decomposition temperature seems to be higher at 245 °C (Fig. 15).



Scheme 1

[Cu_5Cl_5 (Si(O–CH_2–CH=CH_2)$_4$) (**16**) is the first reported example of a organo-silicon olefin–copper(I) coordination polymer prepared by reacting tetraallyloxysilane with CuCl.[15] In the structure, the tetraallyloxysilane ligand is tetradentate which gives a 4-fold axis passing through the Si atoms of the ligand. The four copper centers are linked by four Cl atoms to form an eight-membered ring and the remaining copper is connected to the four Cl atoms of the eight-membered ring and to a Cl in an axial position perpendicular to the plane of the eight-membered ring to give an approximately pyramidal coordination geometry (Fig. 16). Each [Cu_5Cl_5] cluster connecting node is linked to four tetraallyloxysilanes to result in the formation of a 2D layered framework (Fig. 16).

[Cu_3Br_4(triallylguanidinium)] (**17**) was prepared under *AC* electrochemical conditions.[16] The trigonal-pyramidal coordination sphere of the copper atom comprises three halogen atoms and a C=C double bond moiety in the equatorial plane. The inorganic $Cu_3Br_4^-$ anions are positioned along 3 axes and combined with triallylguanidinium cations into layers by the Cu–(C=C) interactions. The triallylguanidiniu tridentate ligand results in the formation of a 2D framework with the Cu_3Br_4 clusters as connecting node (Fig. 17).

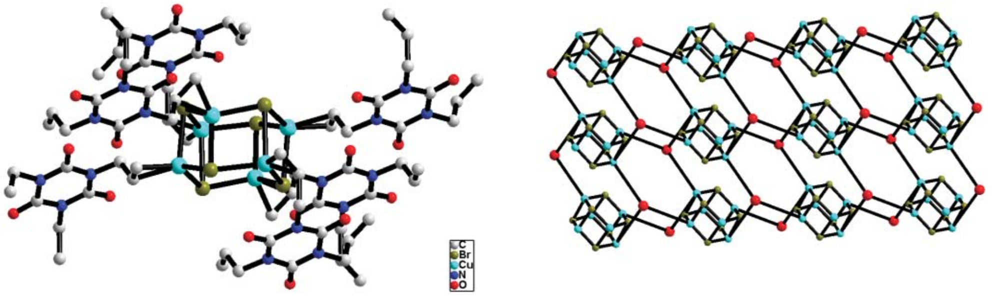


Fig. 13 An asymmetric unit of compound **13** (left) and simplified 2D grid network representation of **13** (right).  stands for TTT.

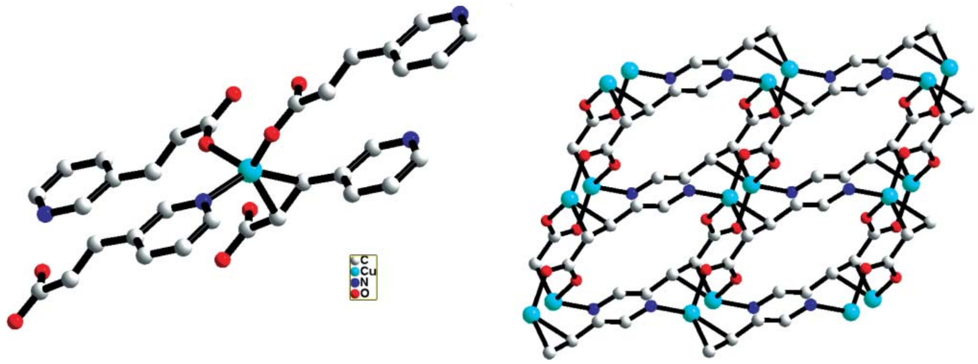
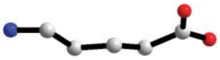


Fig. 14 An asymmetric unit compound of **14** (left) and simplified 2D grid network representation of **14** (right).  stands for anion 3-PYA

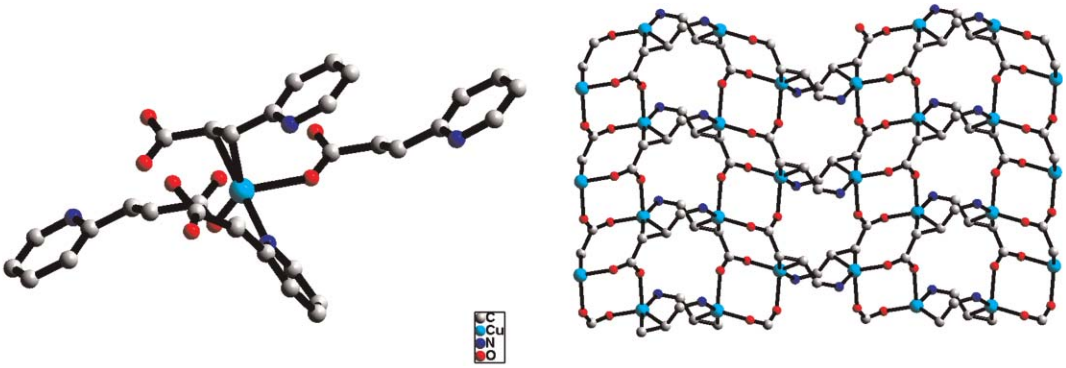
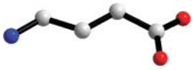


Fig. 15 An asymmetric unit of compound **15** (left) and simplified 2D grid network representation of **15** (right).  stands for cation 2-PYA

[CuCl(4-vinylpyridine)]$_n$ (**18**) was synthesized under hydrothermal conditions through the reaction between CuCl and 4-vinylpyridine (4-VPY).[17] The X-ray crystal analysis of complex **18** reveals the Cu(I) ion in **18** to be coordinated in a distorted tetrahedral geometry, which is defined by two chloride atoms and one nitrogen atom and the C=C moiety of the olefin. The 4-VPY ligand acts as bidentate spacer that links two Cu atoms. The Cl atom also bridges two Cu atoms, which leads to the formation of a 2-D framework; the framework is wall-brick net type. Each rectangular net in **18** has an approximate dimension of 10.576–7.322 Å. It is interesting to note that the two longer sides of each rectangle contain a Cu_2Cl_2 dimer moiety (Fig. 18). This suggests that the cavity can intercalate or include a guest molecule. The packing view shows that the two adjacent layers are in a staggered arrangement and adopt an AB type layer.

[CuCl(1-allylbenzotriazole)]$_n$ (**19**) was obtained under *AC* electrochemical conditions. Coordination of Cu(I) atoms

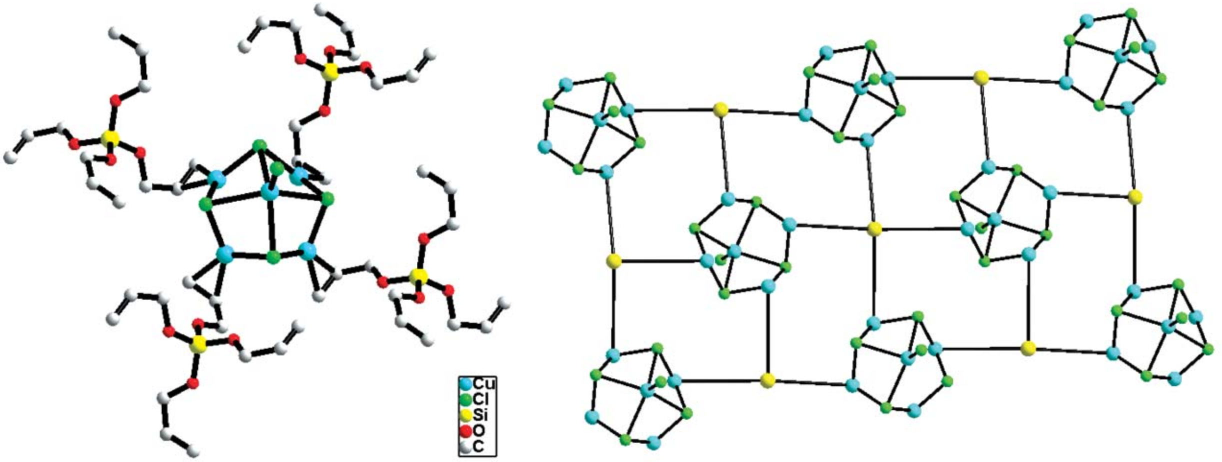
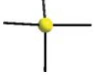


Fig. 16 An asymmetric unit compound of **16** (left) and simplified 2D grid network representation of **16** (right).  stands for Si(O–CH_2–CH=CH_2)$_4$.

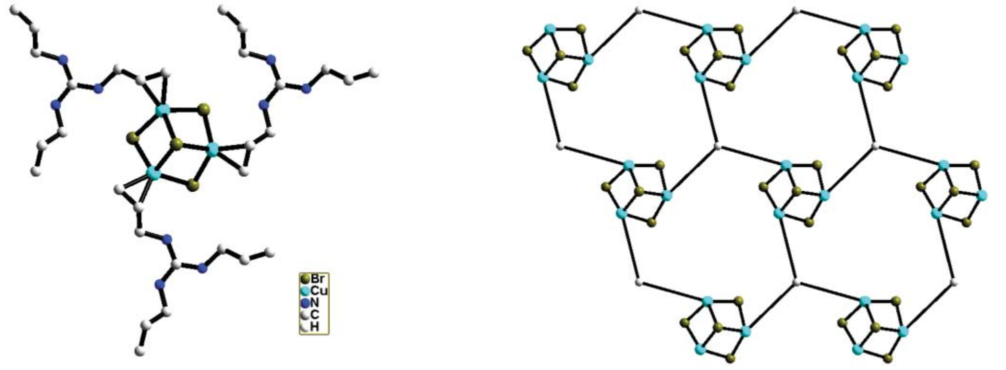


Fig. 17 An asymmetric unit compound of **17** (left) and simplified 2D grid network representation of **17** (right).  stands for triallylguanidinium.

through the nitrogen atom and olefinic group of the same molecule results in the appearance of organometallic chains. Bridged Cl atoms combine these chains into a 2D brick-wall layered framework (Fig. 19) The trigonal-pyramidal copper environment involves two Cl atoms (one of them occupying the apical position), a nitrogen atom and a C=C moiety.[18]

[Cu_2Br_2Cl(*N*,*N*′-biallyl-*S*-ethylisothiouronium)] (**20**) consists of 2D infinite coordination layers with six-membered rings linking distorted fourteen-membered rings as connecting node. Four Cu_2Br_2 dimers linked by two Cl atoms and two ligands form the fourteen-membered ring. Sharing two Cu atoms and one ligand with adjoining fourteen-membered ring, the six-membered ring is completed by four Cu atoms linked to two Cl atoms. This results in the formation of a 2D framework as shown in Fig. 20.[19]

[Cu_3Br_2(diallylamine)]$_n$ (**21**) with an unusually high CuX:diallylamine ratio was obtained by *AC* electrochemical synthesis. A molecule of diallylamine attaches to three copper(I) atoms of the same inorganic fragment with the copper atoms having different coordination spheres: Cu(1) possesses trigonal planar coordination formed by two halide atoms and C=C bond, Cu(2) occupies a trigonal pyramid

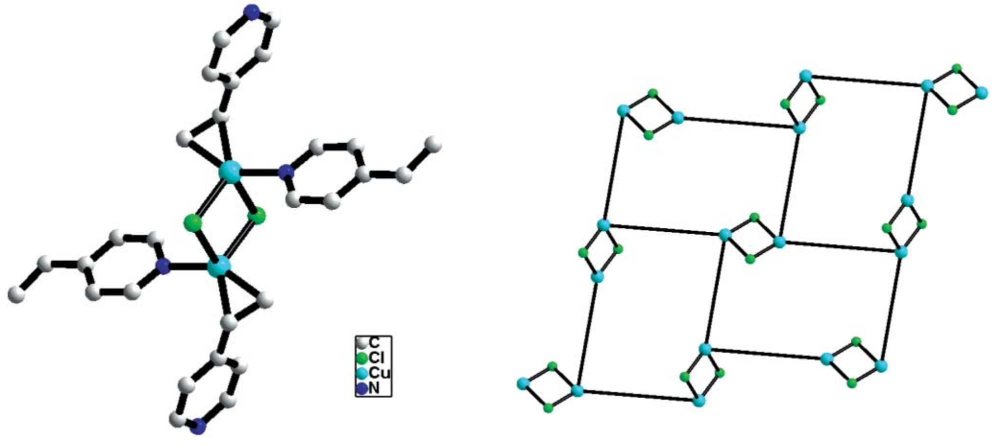


Fig. 18 An asymmetric unit compound of **18** (left) and simplified 2D grid network representation of **18** (right). The long straight line stands for 4-vinylpyridine.

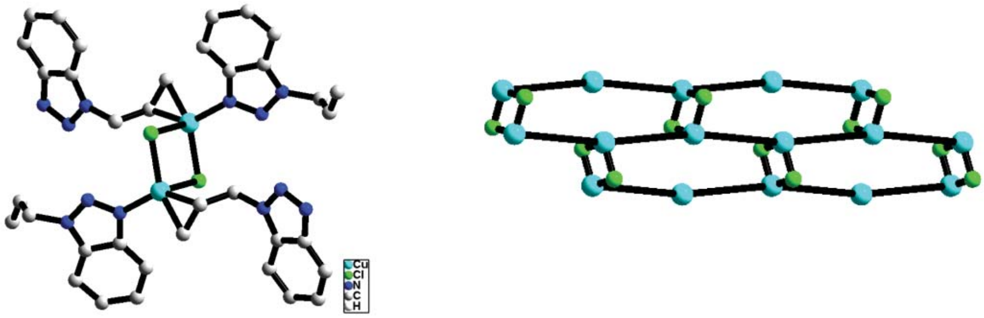


Fig. 19 An asymmetric unit compound of **19** (left) and simplified 2D grid network representation of **19** (right). The long straight line stands for 1-allylbenzotriazole.

coordination sphere that is completed by the coordination of an additional halide atom, whereas Cu(3) is tetrahedral with three halide atoms and one nitrogen atom to result in the formation of a 2D layered framework (Fig. 21). It is notable that the olefin ligands are located on the two sides of the framework.[20]

Finally, [Cu (allylcyanido)(NO_3)] (**22**) is a 2D infinite highly undulated layers consisting of hexagonal units similar to hexamethylene with each containing six Cu atoms and six olefin ligands as spacers (Fig. 22).[21]

2.5 Homochiral two-dimensional olefin–copper(I) coordination polymer motifs

Homochiral coordination polymers where all crystals have the same handedness provide the added advantage of offering applications in heterogeneous asymmetric catalysis and enantioselective separation. Three homochiral olefin–copper(I) coordination polymers have been previously reported to be prepared under solvothermal reaction conditions, of which only one is known to be capable of exhibiting enantio-intercalation of racemic molecules. To the best of our knowledge, there are three common coordination polymers with enantioseparation effect. However, a successful access to an enantio-resolvable zeolite analogue composed of olefin–copper polymer remains a challenge.

[Cu_8X_{10}(H-quinine)$_2$] (X = Cl, Br) (**23**, **24**) are the first reported examples of two homochiral 2D infinite layered olefin–copper(I) coordination polymers with complicated $[Cu_8X_{10}]^{2-}$ cluster as connecting node.[22] The terminal copper

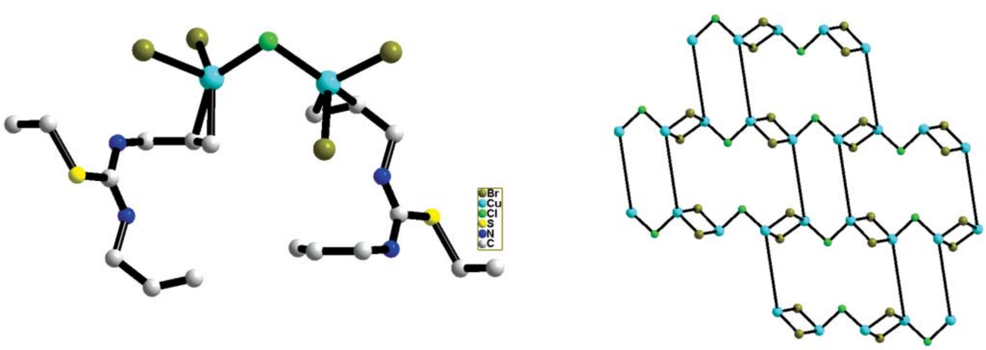


Fig. 20 An asymmetric unit of compound of **20** (left) and simplified 2D grid network representation of **20** (right). The long straight line stands for *N*,*N*′-biallyl-*S*-ethylisothiouronium.

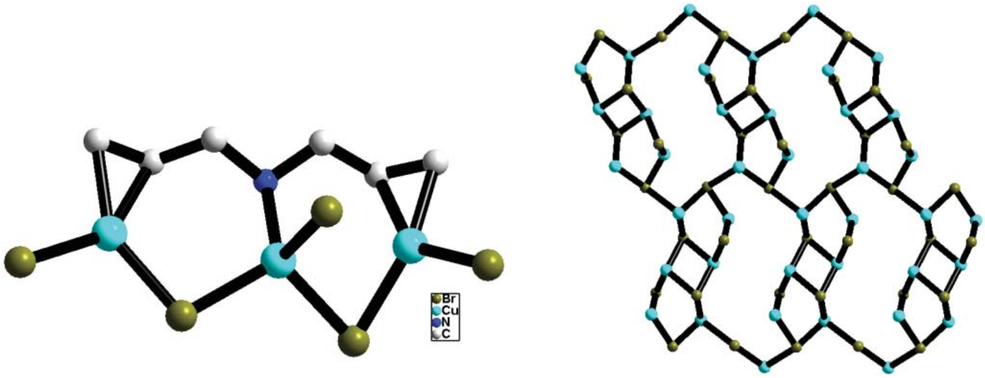


Fig. 21 An asymmetric unit of compound of **21** (left) and simplified 2D grid network representation of **21** (right).

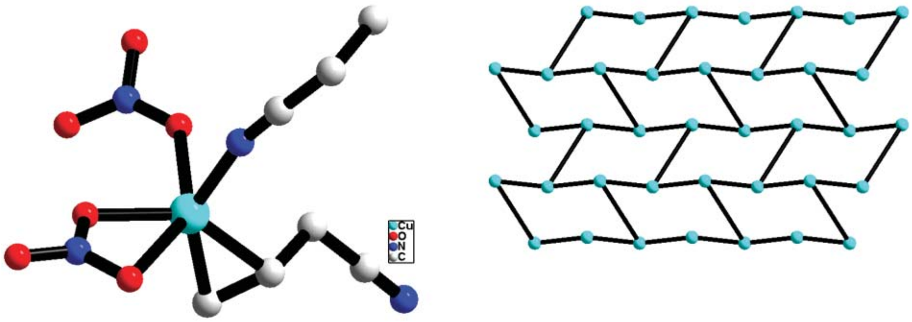


Fig. 22 An asymmetric unit of compound **22** (left) and simplified 2D grid network representation of **22** (right). The long straight and short lines stand for allylcyanido ligand and nitrate, respectively.

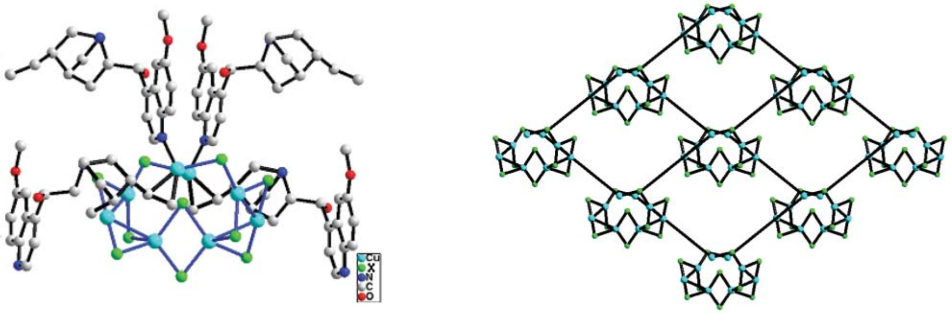


Fig. 23 An asymmetric unit of compound **23** (left) and **24** and simplified 2D grid network representations of **23** and **24** (right). The long straight line stands for a quinine ligand.

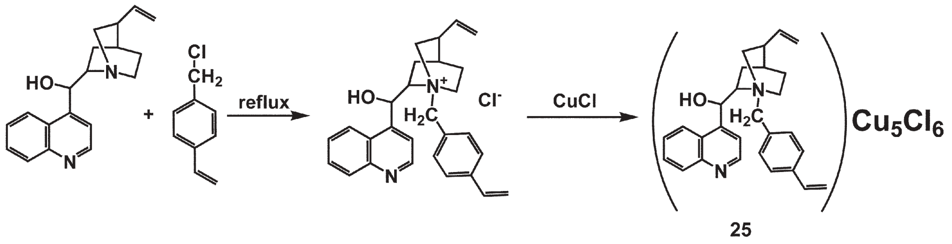
centers are coordinated by a quinoline nitrogen of one H-quinine, a C=C moiety of another H-quinine and a bridging chloride ion. The remaining copper centers form an approximate trigonal pyramidal coordination environment with linear coordination of the chloride ions. An unusual feature of this anion is the sharp kink at one of the Cl atoms. Each $[Cu_8X_{10}]^{2-}$aggregate is linked to four other equivalent aggregates through the bridging H-quinines, resulting in the formation of a 2D layered network (Fig. 23). The arrangement of adjacent layers of the 2D network is AA type packing.

Cu_5Cl_6(VB–N–CIN)·C_2H_5OH (**25**·EtOH) (**25**) was prepared by the reaction of chiral phase transfer catalyst vinylbenzylcinchonidinium chloride ([VB–N–CIN]Cl), which can be prepared from the corresponding cinchona alkaloid, with CuCl under solvothermal conditions (Scheme 2).[23] Compound **25** is an unprecedented example of a 2D layered homochiral Cu(I)–olefin coordination polymer. The five Cu(I) centers connect together by four μ_2-Cl and two μ_3-Cl linkers which results in the formation of two clusters composed of two triangles with the two triangles sharing a common Cu corner. The four Cu atoms are all three-coordinated and coordinate to the N atom of the quinoline ring and olefin moiety of the quinuclidine ring to give a 2D square-grid network. The Cu corner coordinates to four Cl atoms to give a tetrahedral geometry. It is noteworthy that the two adjacent layers are not in a staggered arrangement but adopt an AA type arrangement. It is clear that one ethanol molecule is intercalated between two layers of **25** in the framework (Fig. 24).

2.6 Three-dimension motifs

There is only one 3D coordination polymer that has been reported in recent years despite the propest of self-assembly of the olefin ligands with the coordinative flexible Cu(I) atoms providing interesting molecular architectures.

The structure of $Cu_2(O_2CCH{=}CHCO_2)$ (**26**) exhibits common geometric motifs in a unique structure type.[24] The structure consists of four unique crystallographic entities that involve the Cu centers forming a complicated layered structure. Each layer is comprised of parallel copper fumarate chains that are linked in two directions to give a 2D copper fumarate network. The first and third tiers are symmetry-equivalent. Each tier contains eight-membered rings that contain O–Cu–O bonds, and the copper atoms are also



Scheme 2

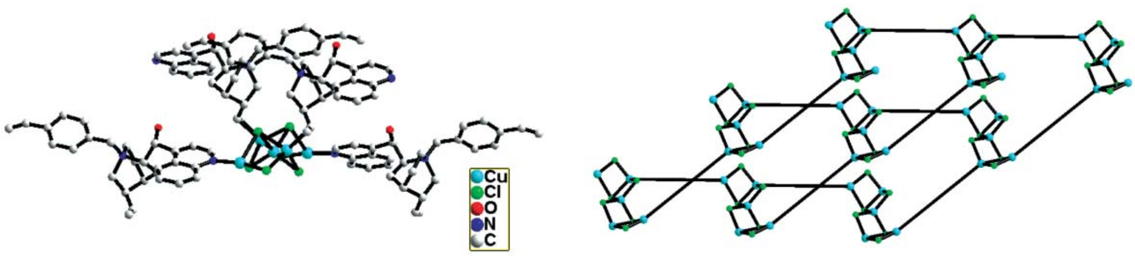


Fig. 24 An asymmetric unit of compound **25** (left) and simplified 2D grid network representation of **25** (right) in which each grid node is composed of two Cu–Cu–Cu triangle clusters. The long straight line stands for cation vinylbenzylcinchonidinium.

bonded to ethylene substituents of neighboring chains (above the plane of the rings), to afford a 3D copper fumarate network. There is a gap of approximately 3.0 Å between the neighboring three-tiered layers along the *c*-axis direction. This is a very complicated 3D network with an unprecedented topological motif (Fig. 25).

Finally, we can list $Cu_nX_m^{n-m}$ cluster as connecting node in Table 1 in which it is notable that almost $Cu_nX_m^{n-m}$ clusters can be regarded as dimer (Cu_2X_2) aggregates.

3 Applications of olefin–Cu(I) coordination oligomers and polymers

An attractive feature of highly stable olefin–Cu(I) coordination polymers is their suitability for various functional applications. Functionalities can be readily introduced onto the metallosupramolecular structure by employing functional olefins in the assembly processes. Upon metallosupramolecular structure formation these functions may interact, leading to a higher level of functionality. On the other hand, olefin–Cu(I) coordination polymers containing Cu(I) ions are generally more sensitive and responsive to electro- and photochemical stimuli compared to metal-free olefin molecules. Therefore, the employment of highly stable olefin–Cu(I) coordination polymers may open up new opportunities to develop novel molecular switches and devices. Highly stable olefin–Cu(I) coordination polymers have been applied to various fields of science and technology. A selection of functional olefin–Cu(I) coordination polymers and their applications are highlighted in the following sections.

3.1 Electrochemical properties

Cu(I)–olefin coordination oligomers and polymers are an excellent choice for probing electron-transfer processes at an electrode surface owing to the considerable stability of Cu(I) cations. In this context, compounds **1**, **2** and **3** not only possess high thermal stability, but also fascinating redox behavior. The cyclic voltammograms of CuCl, compounds **1–3** reveal one oxidation peak and a similar cathodic wave in the sweep range from +300 to −1100 mV. Their anodic peak potentials are −308, −300, −290, and −278 mV at 100 mV s^{-1}, respectively. No peaks were observable in a solution containing only the ligand, which suggests that the anodic peaks were attributed to metal-centered oxidation. The single oxidation peak indicates that two metal centers in the complexes are in the same local

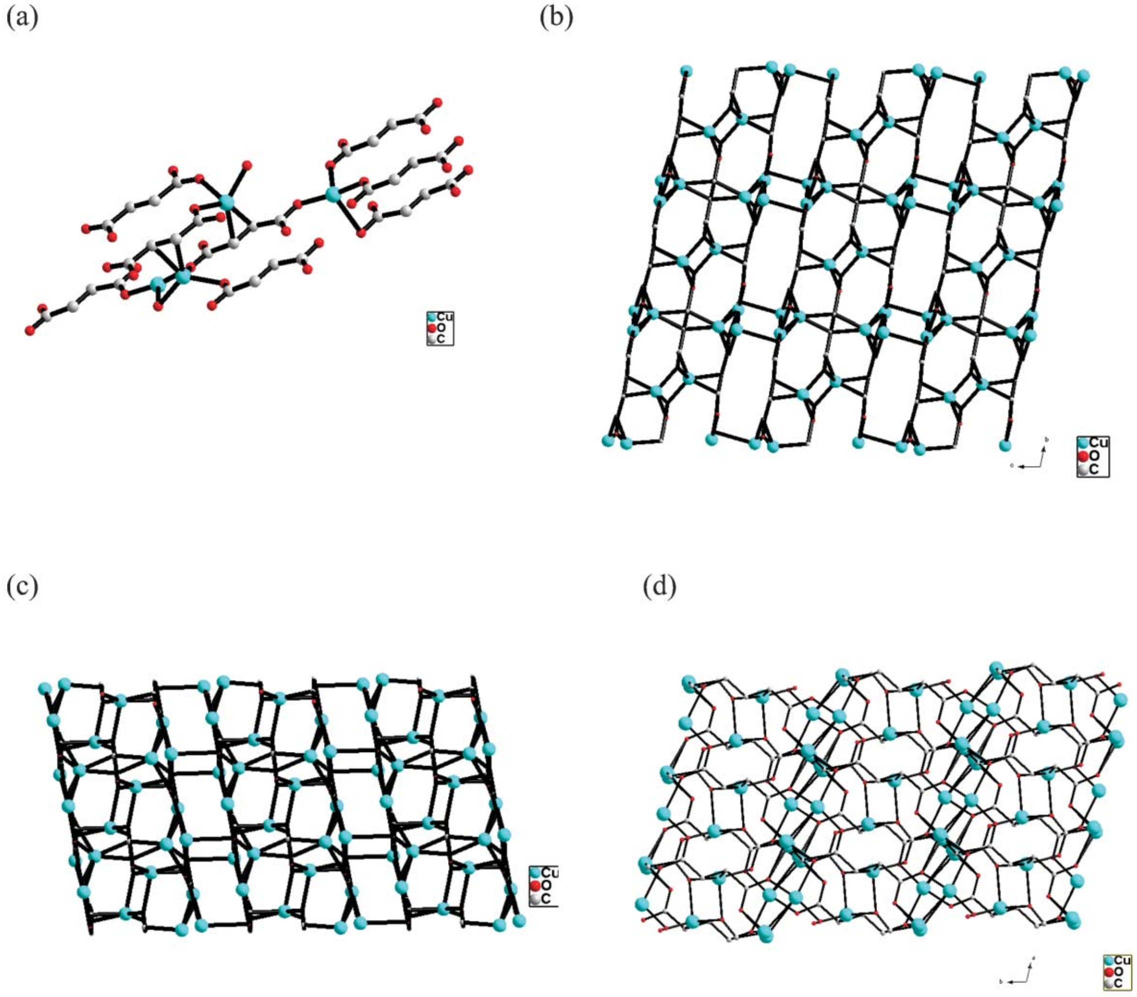


Fig. 25 (a) An asymmetric unit of compound **26** and 3D copper fumarate network representation from (b) (along *a*-axis),(c) (along *b*-axis), (d) (along *c*-axis).

Table 1 $Cu_nX_m^{n-m}$ cluster types in multi-dimensional olefin copper(I) coordination oligomers and polymers

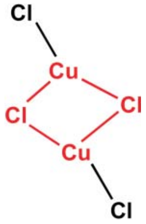
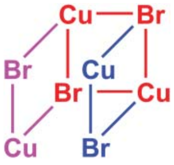
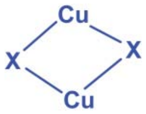
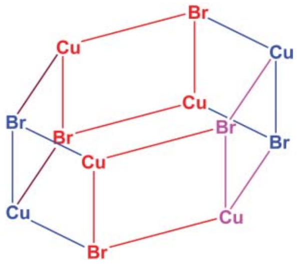
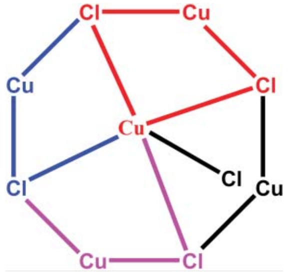
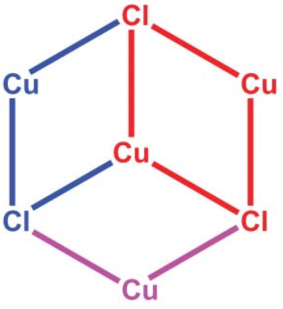
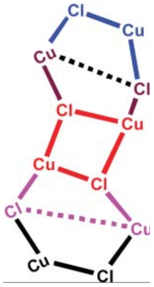
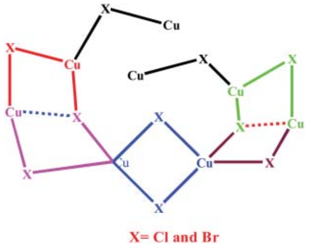
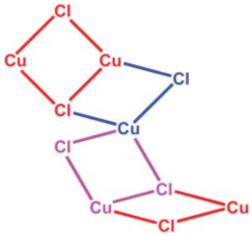
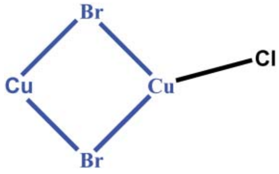
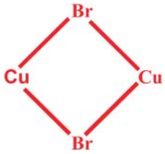
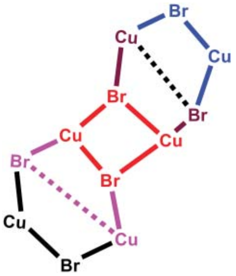
$Cu_nX_m^{n-m}$		Dimer numbers	Connecting mode	Examples	Ref.
n	M				
2	4	1		**1**	5
4	4	3		**10**	11
2	3	1		**11**	12
6	6	6		**13**	11
5	5	4		**16**	15
3	4	3		**17**	16

Table 1 $Cu_nX_m^{n-m}$ cluster types in multi-dimensional olefin copper(I) coordination oligomers and polymers (*Continued*)

$Cu_nX_m^{n-m}$		Dimer numbers	Connecting mode	Examples	Ref.
n	M				
3	4	5		**12**	13
8	10	5		**23**, **24**	22
5	6	4		**25**	23
2	3	1		**20**	19
2	2	1		**19**	18
6	6	5		**21**	20

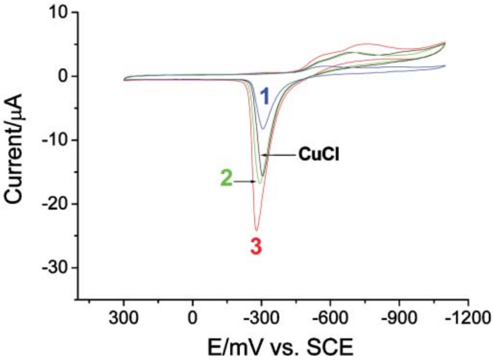


Fig. 26 Cyclic voltammograms of 0.1 M Bu_4NClO_4 acetonitrile solutions containing 1.0 mM CuCl, (**1**),(**2**), and (**3**) at 100 mV s^{-1} at a platinum disk working electrode.

coordination geometry. The cathodic peaks are assignable to reduction of Cu(I) to Cu. Taking into consideration that there are two metal centers in these complexes, the peak current of CuCl per mole is larger than those observed for compounds **1**–**3** (Fig. 26). The greater positive anodic peak potentials and lower peak currents found in **1–3** than those of CuCl could be due to the H_2PYA^+ ligands. The decrease in anodic peak current could be due to a smaller diffusion coefficient in these complexes. The resulting difference between the peak potentials of the three complexes may be due to different steady constants.

Similarly, compounds **10** and **13** not only exhibit highly thermal stable properties, but also have fascinating redox behavior. Electrochemical measurements with platinum and glassy carbon working electrodes gave similar results for these compounds. The cyclic voltammograms show that both compounds **10** and **13** display one redox couple with similar behaviors, which is indicative of closely related structures. The anodic and cathodic peak potentials of **10** were −146 and −530 mV at 150 mV s^{-1}, respectively, while the peaks of **13** occurring at −166 and −530 mV. No peaks were observed in a solution containing only the ligand, which suggests that these peaks were attributed to metal-centred oxidation and reduction. The single oxidation peak for both complexes indicated that all of the Cu(I) centers were in the same local coordination environment. The linear relation between peak currents and the square root of the scan rate, the large difference between anodic and cathodic peak currents, and the large peak-to-peak separations all indicated that both electrode reactions were irreversible processes. The larger peak current of **10** to that of **13**, was caused by a higher solution concentration of **10** in acetonitrile. A smaller peak-to-peak separation of **13** to that of **10** and a larger ratio of peak current to amount of Cu(I) centers in solution indicate a more rapid electron-transfer rate in **13**, as a result of its prismane based structure (Fig. 27).

Due to the structural features of olefin–Cu(I) coordination oligomers and polymers, some of them have molecular square topological structure.[25] Consequently, this combination of electroactivity and structure makes olefin–Cu(I) coordination oligomers and polymers attractive as sensory materials.

3.2 Fluorescent sensing

Luminescence in first-row transition metal complexes is frequently by-passed by the presence of lowering ligand-field excited states (ES) which may be too short-lived to have measurable emissions. On the other hand, filled-shell d^{10} systems offer an opportunity to observe other excited states. Olefin–Cu(I) coordination polymers containing Cu^+ ions with filled-shell d^{10} systems and olefin ligand can combine to give π-bonded systems. As we can see from the structures discussed earlier, olefin–Cu(I) coordination polymers are usually polynuclear compounds which are a common feature with the mixing of states. As a consequence, assigning ES with concepts drawn from simple one electron transitions may be quite misleading and short copper–copper distances strongly influence the energies of the luminescent active states. The low-energy band could be assigned to a metal-to-ligand charge transfer (MLCT) but the copper metal center d to s orbital transition cannot be ruled out. The short luminescent lifetime of those coordination polymers in the solid state suggests their emission should be fluorescent emission.[26]

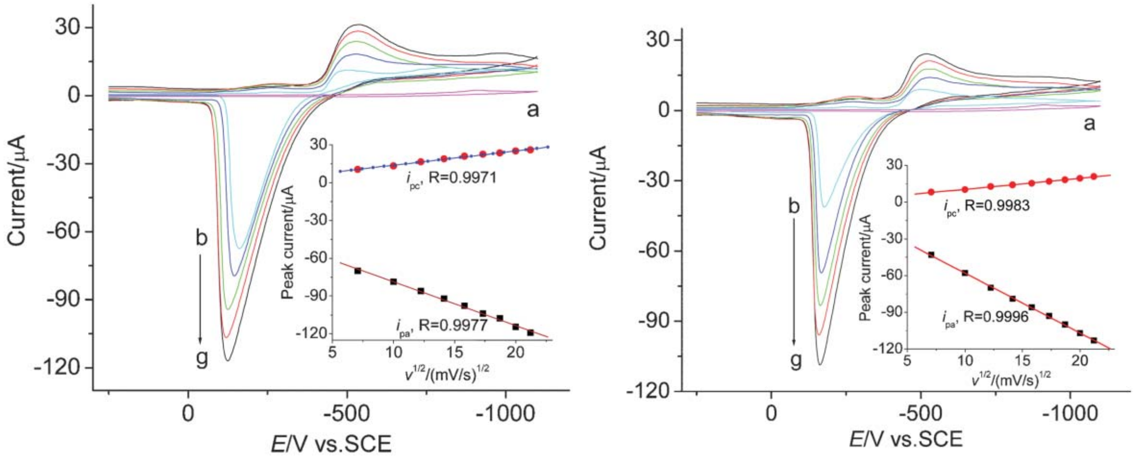


Fig. 27 Cyclic voltammagrams of 1.0 mm TTT in 0.1M Bu_4NClO_4 solution (CH_3CN) at 150 m Vs^{-1} of 1.0 mm of **10** (left) and 0.5 mm of **13** (right) in 0.1M Bu_4NClO_4 solution (CH_3CN) at 50, 150, 250, 350, and 450 mV s^{-1}(from b to g) at a platinum disc working electrode. Insert: plots of anodic and cathodic peak currents *versus* $V^{1/2}$.

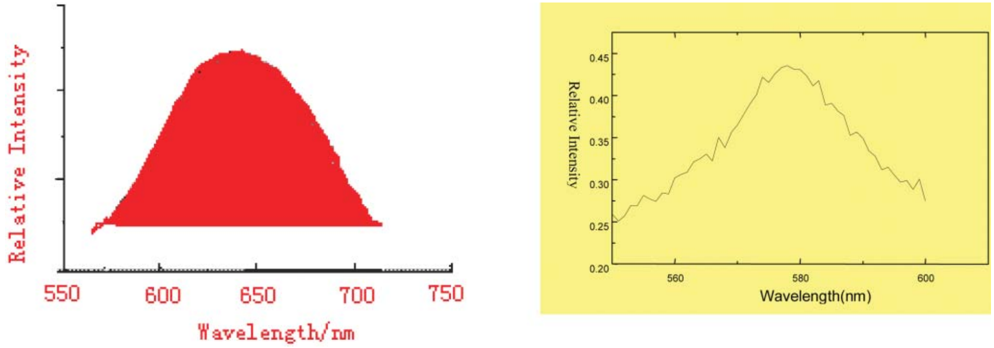


Fig. 28 Fluorescent emission spectrum of **6** (left) and **14**, **15** (right) in the solid state at room temperature.

Compound **6** displays a strong red fluorescent emission in the solid state at room temperature with a maximum at *ca.* 647 nm (λexc = 250 nm) (Fig. 28a). Its diffuse reflectance UV-VIS spectrum shows a low-energy band at *ca.* 429 nm, which can be assigned to the metal-to-ligand charge transfer (MLCT) band. A clearly bathochromic shift occurs in **6** relative to [Cu_4I_4(py)] (λemax = 580 nm) and [Cu(3,4-bpyBr)] (λemax = 580 nm) which is probably due to π-back-donation from the filled metal dπ orbital to the vacant antibonding π* orbital of the coordinated olefin.

Compounds **14** and **15** display yellow fluorescent emission in the solid state (Fig. 28b). Their diffuse reflectance UV-vis spectra clearly indicate one high energy band at *ca*. 275 nm for **14** and 330 nm for **15** and one low-energy band at *ca*. 404 nm for **14** and 406 nm for **15**. The former may be assigned to intraligand transition of the free ligand due to 3-HPYA and 2-HPYA having a band at similar wavelengths (280 nm for 3-HPYA and 310 nm for 2-HPYA), while the low-energy band should be assigned to a metal-to-ligand charge transfer (MLCT). However, the metal center d to s orbital transition cannot be ruled out. This suggests that the emission at 580 nm in **14** and **15** can be tentatively ascribed to MLCT since the fluorescent emission of free ligand in the solid state is observed at 375 nm for 3-HPYA and 382 nm for 2-HPYA, respectively. In addition, the short luminescent lifetime of **14** (*ca.* τ = 1.06 ns) and **15** (*ca.* τ = 0.96 ns) in the solid state suggests their emission should be fluorescent emission.

Interestingly, compound **18** exhibits a strong yellow fluorescent emission. However, its luminescence can be quenched in an atmosphere of CO (carbon monoxide), probably suggesting that **18** reacts with CO to give an unstable intermediate, presumably Cu(CO)Cl(4-vinylpyridine). However, the intermediate can be converted into **18** (and its luminescence can be recovered) after heating since CO is very labile and easily lost. Thus, the luminescent emission makes it a good candidate for sensing applications on the basis of recognition and inclusion of appropriate guest molecules (Fig. 29).

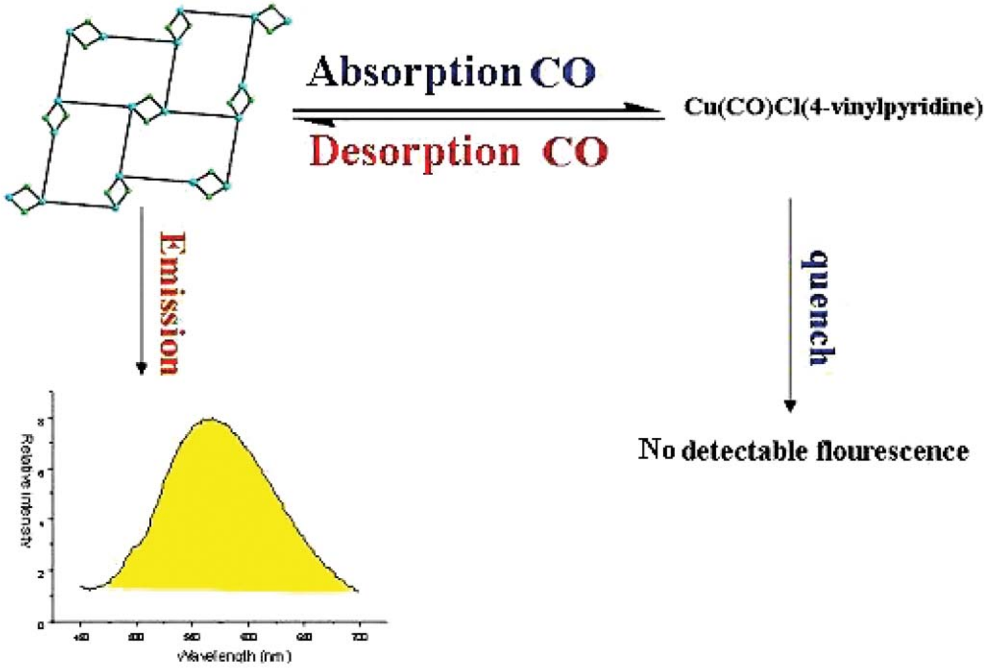


Fig. 29 Proposed process by compound **18** absorption and desorption of CO, and its fluorescent emission spectrum in the solid state at room temperature.

3.3 Ferroelectric properties

Recently, ferroelectric behavior is particularly desirable, and materials exhibiting this behavior are the focus of intense studies because of the possibility to switch rapidly between different states by an external electric field. Such materials may be useful in a variety of new technologies such as electric-optical devices, information storage, switchable NLO (non-linear optical) devices, and light modulators.

In crystallography, the 10 polar point groups (C_1, C_s, C_2, C_{2v}, C_3, C_{3v}, C_4, C_{4v}, C_6, C_{6v}) are required for ferroelectric behavior. In recent years, a significant amount of effort has been placed on developing ferroelectric coordination polymers[27] and organic compounds[28]. However, olefin copper coordination polymers with ferroelectric property remain very rare.

Homochiral compounds **23** and **24** with 2D layered olefin–Cu(I) coordination polymers prepared by the reaction of quinine with CuX under solvothermal conditions crystallized in a chiral space group *C*2 which is associated with the point group C_2. The experimental results indicate that **23** does indeed display good ferroelectric behavior. An electric hysteresis loop (a typical ferroelectric feature) is produced by compound **23** (Fig. 30), with a remnant polarization (P_r) of 0.12 μC cm^{-2} and a coercive field (E_c) of 5.0 kV cm^{-1}. The saturation spontaneous polarization (P_s) of (**23**) is *ca.* 3.0 μC cm^{-2} compared to 5.0 μC cm^{-2} for ferroelectric KDP. Compound **23** is the first homochiral olefin–Cu(I) coordination polymer exhibiting ferroelectric behavior.

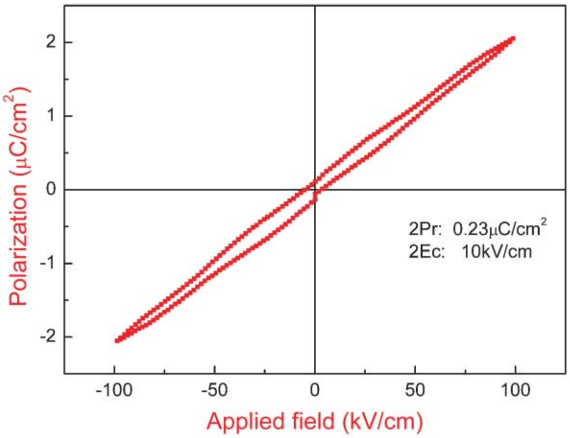
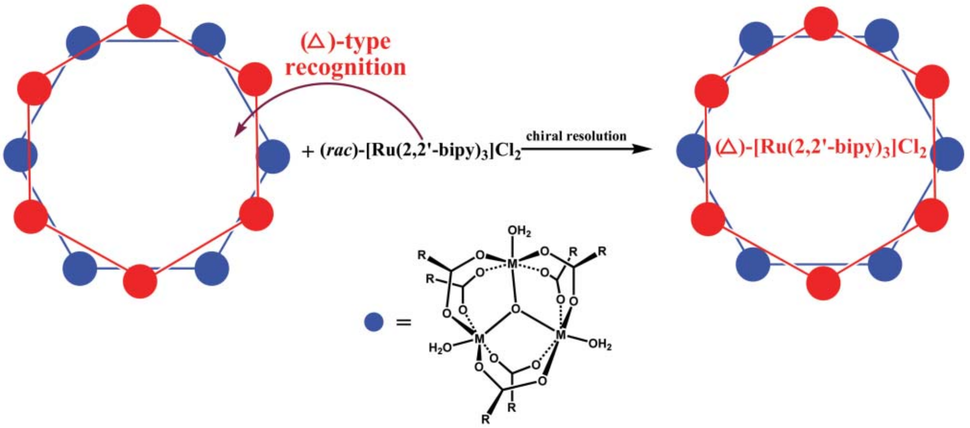


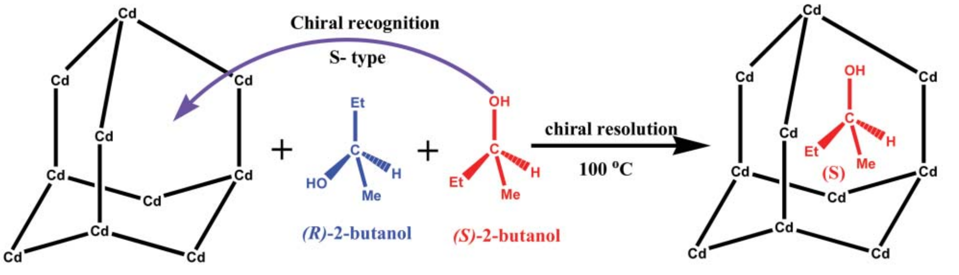
Fig. 30 Electric hysteresis loop of **23** in the form of a pellet, obtained in Virtual Ground Mode at room temperature.

3.4 Chiral separation

The rational design and construction of hybrid organic–inorganic zeolite analogues for enantioseparation and catalysis is of intense current interest. The inclusion of enantiomerically pure homochiral building blocks into microporous materials (zeotypes) for enantiomer separation as well as chiral synthesis and catalysis, has been a continuing challenge and represents an ambitious goal for chemists. Currently, known materials capable of offering enantiomeric separation and catalysis tend to be 2D layered-type structures that are able to intercalate guests. Kim[29] reported a chiral two-dimensional (2D) infinite layer coordination polymer consisting of large edge-sharing chair-shaped hexagons used for the resolution of [Ru(2,2′-bipy)3]Cl$_2$ (bipy = bipyridine) with the colour of the compound changing from white to reddish yellow. (The ee value was estimated to be approximately 66%.) (Scheme 3). We[30] reported the first 3D homochiral coordination polymer (or zeolite analogue) used for the resolution of a racemic 2-butanol (*ca.* 98.2% for *S*-2-butanol) and 2-methyl-1-butanol (*ca.* 98.4% ee for *S*-2-methyl-1-butanol) (Scheme 4). Lin[31] and co-workers reported a homochiral 2D coordination polymer with lamellar structure used for the resolution of racemic *trans*-1,2-diaminocyclohexane gave an enantio-enrichment of 13.6% in *S,S*-1,2-diaminocyclohexane in the beginning fractions and an enantio-enrichment of 10% in *R,R*-1,2-diaminocyclohexane in the ending fractions (Scheme 5). Chiral recognition in the coordination of olefins to chiral transition metal fragments is a topic of interest, especially in relation to metal-promoted enantioselective syntheses. Although binding selectivity is often not the controlling factor in metal-catalyzed asymmetric reactions, it is more likely to be so in stoichiometric processes.



Scheme 3 Inclusion of (Δ)-[Ru(2,2′-bipy)$_3$]Cl$_2$ in the cavities of [Zn$_3$(μ$_3$-O)(L-H)$_6$·2(H$_3$O)](12H$_2$O) (L = $C_{12}H_{12}N_2O_5$). The red and blue hexagons represent different layers respectively.



Scheme 4 Inclusion of (*S*)-2-butanol in the adamantane-like cavities of Cd(Q–COO)$_2$ (straight line = Q–COO = quitenine).

Compound **25** is a 2D layered homochiral Cu(I)–olefin coordination polymer. It is noteworthy that two adjacent layers are in an AA type arrangement and one ethanol molecule is intercalated between the layers of **25** (Fig. 31). A preliminary enantioseparation investigation shows that the 2D layered network in **25** is capable of selectively intercalating (*R*)-2-butanol with an approximately estimated ee of 25%. This is the first example of a homochiral olefin–copper coordination polymer, which may be useful for enantioseparation although the olefin–copper(I) compounds with chiral ligands can be used for the resolution of racemic mixtures of olefins,[32] proposed resolution process by intercalation as shown in Scheme 6.

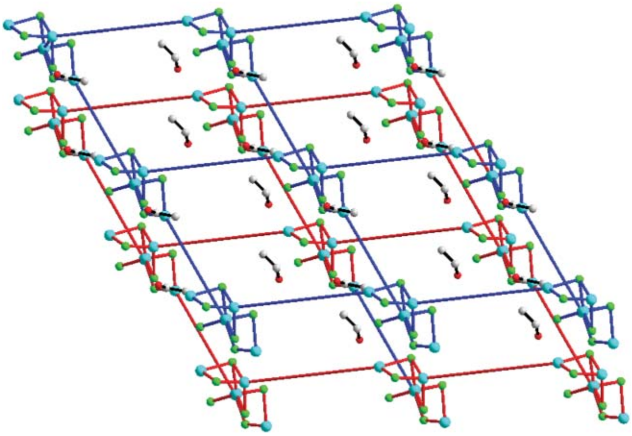


Fig. 31 Packing arrangement representation of the two adjacent layers in **25** showing that ethanol molecules are intercalated between two layers. The long straight line stands for ligand. The red lines and blue lines represent different layers respectively.

4. Summary

Significant progress has been made over the past years in the area of highly stable Cu(I)–olefin coordination oligomers and polymers. Herein we have presented a brief overview on the structure motifs and functional properties of highly stable Cu(I)–olefin coordination oligomers and polymers. Simple copper(I) ions and olefin ligand have been demonstrated to be useful in the construction of intriguing coordination polymeric architectures, which is dependent on Cu/X ratios, counterions, additional organic ligands, as well as other reaction and crystallization conditions. It may be expected that novel organometallic materials and interesting molecular architectures with new topologies can be achieved through controlled solid-state design using the olefin–Cu(I) or other metal–ligand systems.

The interaction between olefin and copper(I) centers results in complexes that exhibit a range of useful properties. As a consequence, both coordination and organometallic chemists are continuing to explore the rich and diverse chemistry this system offers with a view to exploit such complexes in a range of applications. Although the area has progressed impressively over the past few decades, there remains wonderful opportunities for further development and future work can be expected to yield novel olefin–copper(I) complexes that may have useful applications.

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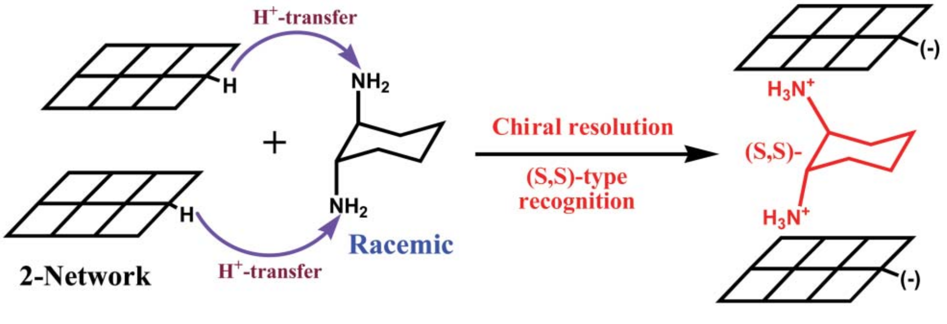

Scheme 5 The proposed chiral resolution process of racemic *trans*-1,2-diaminocyclohexane by [Sm(L-H$_2$)(L-H$_3$)(H$_2$O)$_4$·13H$_2$O (L = 2,2′-diethoxy-1,1′-binaphthalene-6,6′- bisphosphonic acid).

Scheme 6 Proposed resolution process by intercalation.

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