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Metalladiazamacrocycles: Metallamacrocycles as Potential Supramolecular Host System for Small Organic Guest Molecules and Supramolecular Building Blocks for Metal Organic Frameworks

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Metalladiazamacrocycles, coordination driven potential supramolecular host systems, can be obtained via cyclic linkages of the metal ions and the bridging ligands, *N*-acylsalicylhydrazides. The nuclearity and the shape of the metallamacrocycles could be modulated by controlling the steric interactions caused by *N*-acyl tails of the ligands. The macrocycles could be utilized for recognition of small organic guest molecules using their hydrophobicity/hydrophilicity, the size and shape/symmetry of the cavities. In addition, these macrocycles can be used as the supramolecular building blocks for the construction of systematically tuned metal-organic frameworks since these clusters have several replaceable solvent sites which could serve as connecting nodes for the formaton of network structures.

INTRODUCTION

The field of supramolecular chemistry encompasses several areas of chemistry and is, in fact, interdisciplinary in nature. The development of supramolecular chemistry was based on the weak intermolecular forces—mainly interaction other than covalent forces—that are involved in the formation of various assemblies that lead to large and often complicated structures [1–3]. Most of the supramolecules are formed by self-assembly where different subunits of diverse size, shape, functional groups and symmetries are allowed to assemble using a range of weak intermolecular forces under specific and controlled conditions. The forces that are involved in the formation of supramolecular species include hydrogen bonding, ionic, $\pi-\pi$ interactions, and dipole interactions.

Metal-ligand interaction, which is stronger than conventional weak interactions mentioned above, yet weaker than covalent bonding, could be considered as another significant supramolecular interaction for the formation of supramolecular architectures where it can substitute multiple weak interactions for effective directional organization of several molecular building units [4–7]. Assemblies formed by metal-ligand interactions, referred to as metal-organic assemblies, have gained their place in the field of supramolecular chemistry because of a variety of structures they can form and the ability to predict the nature of the final self-assembled product more precisely than the conventional supramolecular species, besides their numerous applications ranging from molecular recognition [8–13], storage [14–19], catalysis [20–24], and single molecular magnets [25–31]. In metal-organic assemblies not only the properties of the ligands but also the properties of the metal ions such as the basicity, coordination geometry and number of available acceptor sites play a crucial role in deciding the nature of the final self-assembled product. The formation of 3-D supramolecular cages from pre-organized ligand units and carefully designed transition metal ions of the desired geometry and

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connectivity was demonstrated [32–34], and the usefulness of the system for stabilization of the reactive intermediate [35–38], as a reaction chamber for a variety of photochemical transformations [39,40], and catalyses [8–13] was established.

While the metal ion provides various geometrical orientations in space it offers a very convenient strategy to direct the ligand binding and therefore allow the formation of specific geometry for the metal-organic assembly. In a metal-organic assembly a metal ion can be considered as a connector that serves as a node and each ligand unit can be considered as a linker. While other auxiliary species, such as capping agents, counter anions/cations and templating agents also play a role in the formation and nature of the final assemblies [4,6,41–46]. As various ligands offer convenient forms of geometry, they are likely to offer a variety of connections resulting in diverse supramolecular architectures. A number of such systems have been dealt with extensively by Fujita *et al.* for 3-D supramolecular metal-organic species [47,48] and Kitagawa *et al.* for

metal-organic frameworks [49]. However, 2-D supramolecular metal-organic species such as metal-lamacrocycle based on organic ligands and metal building blocks had not been considered extensively [32,50,51]. Here we will discuss the work done on a specific category of metallamacrocycles—metalla-diazamacrocycles—and other super structures generated from them, after touching briefly on metallamacrocycles.

Metal Ions as Connecting Nodes for Metallamacrocycles

The formation of metallamacrocycles, where metal ions are the active constituents of macrocyclic rings, requires the metal ions to be the connecting points, referred to as nodes, and the bridging ligands, either linear or of bent geometry, as linkers. The choice of the metal ion and the control of directionality of the metal coordination sites depend on the choice of the final desired macrocycle that is to be assembled (Fig. 1). Linear ditopic connecting nodes such as Au,

(a) Ditopic metal centers and ditopic ligands

(b) Multitopic metal centers and multiple ditopic ligands

(c) Multitopic metal centers and bis-multidentate ligand

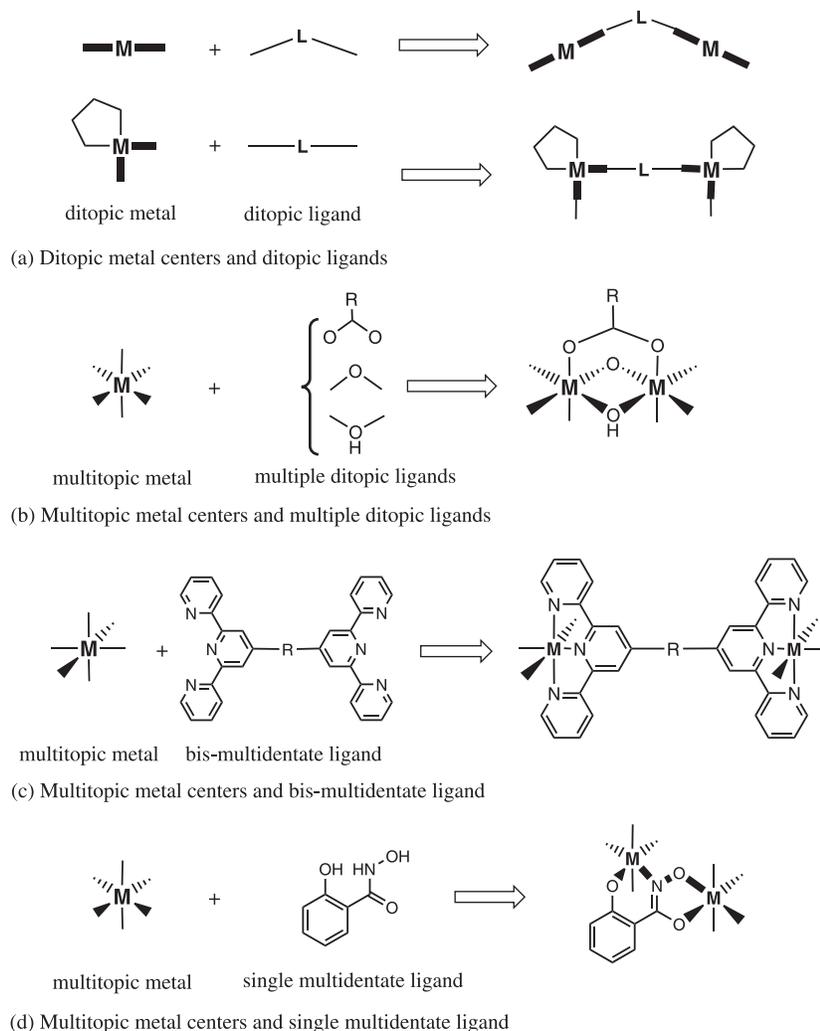(d) Multitopic metal centers and single multidentate ligand

FIGURE 1   Schematic drawings of the types of metal-ligand linkages in metallamacrocycles.

or Ag can be used as potential connecting nodes in macrocycle formation [52,53]. Though Pt, Pd and Cu(I) are usually used as tetratopic nodes and Ru, Rh, Fe, Mn, Co, Cu(II) as pentatopic or hexatopic nodes, these metal centers can be converted to pseudo ditopic nodes that offer two binding sites at an angle of 90° or 180° by using suitable ligand(s) for the selective blockage with specific directional advantage. The combination of the ditopic or pseudo ditopic metal centers with ditopic bridging ligands usually leads to 1-D chain structures. When the ditopic metal centers and ditopic ligands are properly designed, the successive bindings orient the ends of the extending metal-ligand repeats to converge to form a ring, thereby creating a metallamacrocycle (Fig. 1a). For example, the 90° bent ditopic metal centers with rigid linear ditopic ligands lead to molecular squares or molecular rectangles [54–57]. The multitopic metal centers can also be connected using multiple ditopic linker ligands to form the metallamacrocycles (Fig. 1b). Oxides, hydroxides, alkoxides or carboxylates can function as bridging ditopic ligands. The multiple connections of these ligands between the multitopic metal centers generate molecular wheels [58,59]. There are several reports of the use of bis-multi-dentate ligands as dipotic linker ligands (Fig. 1c). The tripyridyl unit of the ligand bound in a meridional fashion to octahedral metal ions such as Fe and Ru can bridge two metal centers to give large metallamacrocycles, where the metal centers serve as pseudo ditopic nodes [60–62]. Compared to these end connected ditopic linkers, reports where a single multidentate ligand acting as a linker leading to macrocyclic structures are sparse (Fig. 1d). One such example is salicylhydroximato ligand that forms various metallamacrocycles with various metal ions [63–66]. The directional nature and peculiar binding preference of the ligand direct a hydroxyl groups to the inner cavity of the macrocycles—termed as

metallacrowns—providing potential binding sites for transition or lanthanide metal ions [66].

METALLADIAZMACROCYCLES

Metalladiazamacrocycles [67,68]—a term coined quite recently due to the presence of an M–N–N metal-diaza backbone—form a class of metallama-crocycles that is an evolved cousin of metallacrowns [63–66]. Since the metalladiazamacrocycles are neutral high molecular mass entities, and have poor solubility in many common organic solvents, establishing their identities by mass spectroscopic methods did not yield convincing results. Therefore X-ray crystallography was used primarily to estab-lish the solid state structure of the compounds in detail. In metalladiazamacrocycles the primary organic species is an N-acylsalicylhydrazide (Figs. 2 and 3). The N-acylsalicylhydrazide has three potential deprotonable sites and five potential donor atoms. The disposition of the donor atoms for tridentate coordination on its one side and bidentate coordination on the other side enables its role as a ditopic linker between two metal centers, while a 'salicyl head domain' and 'N-acyl tail domain' extends out of the 'bridging domain'. Though metalladiazamacrocycles do not posses the property of metallacrowns such as binding transition metal ions or lanthanide ions using hydroximate oxygen donors in the macrocyclic rings, the nuclearity and the shape of the macrocycles could be modulated by tuning the N-acyl tail domain of the ligand.

The steric crowding at the N-acyl tail can be modified by introducing various alkyl or aryl groups of varying steric bulkiness and rigidity in orientation (Fig. 3b). The smallest member of this class of ligand where a hydrogen atom occupies the N-acyl tail—N-formylsalicylhydrazide—forms a hexanuclear metal-
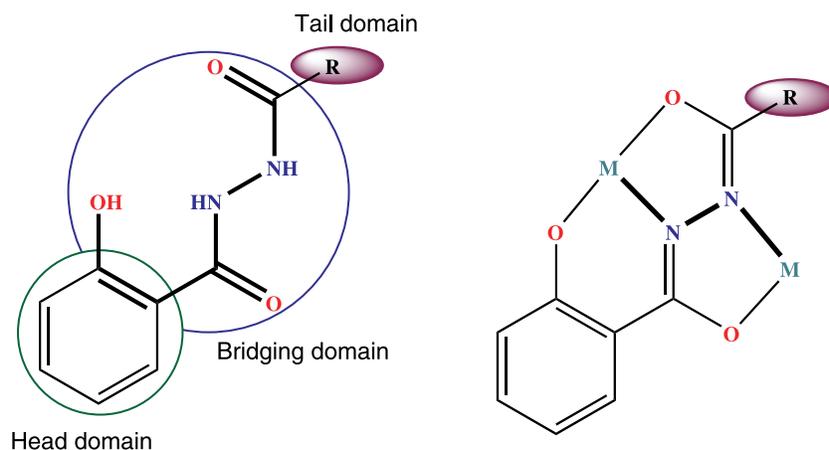

FIGURE 2 Schematic diagrams representing three domains of the ligand, N-acylsalicylhydrazide and its bridging mode.

(a)

H₃xshz

R = Alkyl/Aryl group
S = dmf/dma/MeOH/Py

M = Mn³⁺, Fe³⁺, Co³⁺, Ga³⁺
A representative macrocycle with
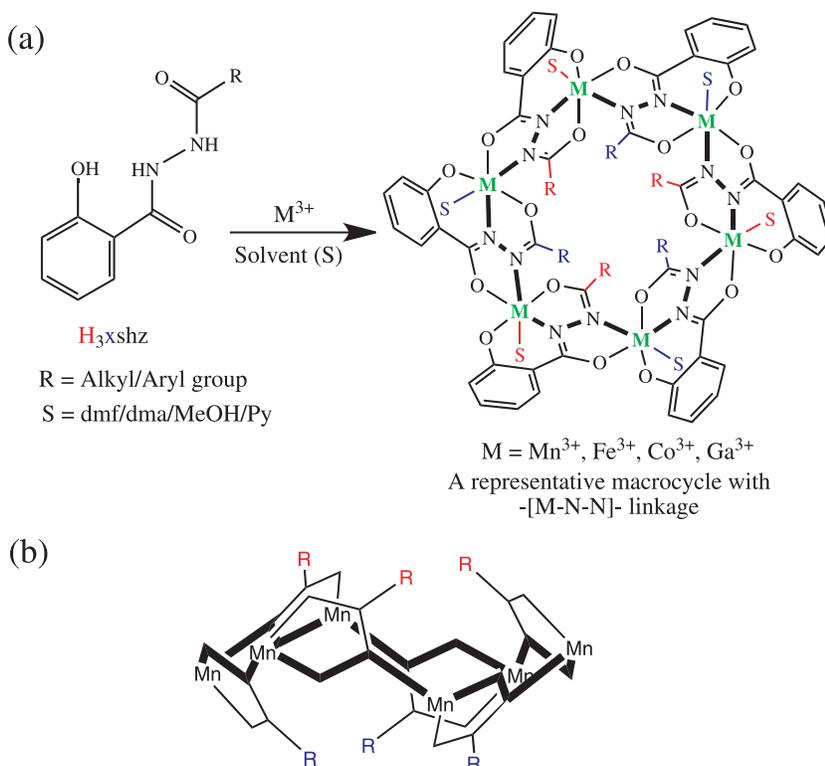-[M-N-N]- linkage

(b)

FIGURE 3   (a) The reaction scheme for the preparation of metalladiazamacrocycles. (b) Schematic side view represents the steric interaction between the *N*-acyl tail domains of the ligands.

ladiazamacrocycle with Mn(III) [69], Co(III) or Ga(III) [70] metal ion where the metal centers are in the alternating chiral configuration, Λ and Δ, because one ligand in tridentate and the other in bidentate binding mode around the metal center are arranged in a propeller fashion (Fig. 4). On modifying the *N*-acyl group by introducing progressively longer alkyl chains such as methyl, ethyl, pentyl and undecyl alkyl groups a series of isostructural hexanuclear structures are formed [71]. An increase in number of carbon atoms does not affect any increase in the nuclearity or nature of the resulting macrocycle. This could be due to the flexibility of the unsubstituted carbon chains about the C—C single bonds of the *N*-acyl tails. All the hexanuclear metalladiazamacrocycles lead to a disc like architecture with ∼2 nm diameter and 1–3 nm thickness. Co(III), Fe(III) and

Ga(III) ions also form similar hexanuclear systems with linear *N*-acylsalicylhydrazides [70]. The variation across the band of various metal ions for the hexanuclear macrocycles is limited to the local variation in the metal coordination environment such as bond length and bond angles. In other words the octahedral coordination environment of gallium, cobalt and iron does not influence any significant changes in the nature of the final product. In another cobalt compound reported by Liu *et al.* replacing the terminal methyl group by an amino group yields a hexanuclear metallamacrocycle [72]. The presence of amino group offers a steric interaction similar to the methyl group but provides hydrogen bonding environment at the core cavity. In fact the macrocycle traps two methanol molecules in the cavity on account of this hydrophilic interior.

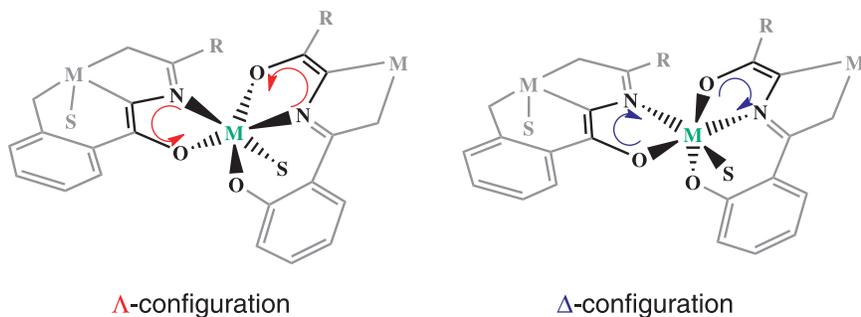Λ-configuration   Δ-configuration

FIGURE 4   Schematic representation of the chiral configuration around metal center.

When vanadium was used as the metal ion for the complexation, even though the binding mode of the ligand is quite similar to that of the metalladiazamacrocycles the successive propagation of the binding was found to be limited. The oxo preference of the vanadium(IV) and/or vanadium(V) centers prevents simultaneous tridentate-bidentate binding around the metal center and leads to trinuclear structure rather than a cyclic structure [73]. Nickel(II) metal ion also prefers trinuclear complex in favorable conditions, where two terminal nickel centers are in a tetra-coordinate square planar geometry, while the central nickel is having a six coordinate octahedral geometry [74–76]. As in the vanadium complex, even though the ligand can bridge the two metal center using the tridentate-bidentate binding mode, further propagation of the same bridges for the cyclic structures cannot be accomplished because the terminal nickel(II) centers get satisfied by a four coordinate square planar geometry probably due to the strong ligand field strength provided by the tridentate chelating donor atoms. This prevents simultaneous tridentate and bidentate bindings around each metal center and interfere with formation of metallamacrocycle.

The solvent molecules that coordinate at the sixth coordination site of the octahedral metal ions in the metallamacrocycle do not have any influence on the structure of the macrocycle [77]. Regardless of the kinds of donor atoms and/or the steric bulkiness of the solvent molecules only the isostructural hexanuclear metalladiazamacrocycles were obtained.

For the purpose of a detailed discussion on the effect of N-acyl substituents on the nuclearity of the metalladiazamacrocycles, we choose manganese based systems as sufficient data is not available

with other metal ions to have a clear idea. The various carbon atoms in N-alkyl tails located at C_3 symmetry related sites interact at the closest (Fig. 5). The existence of close contact interactions at the inner core of the metallamacrocycles prompted us to engineer a modulation of the metallamacrocycle by introducing bulkier N-acyl groups that offer increased steric crowding. The strategy involves introducing substituents with gradually increasing size at important locations in the N-acyl chain or geometrically restricting the rotation of the chain about the C—C bond. As an attempt methyl/dimethyl/phenyl substituents were introduced at the β-position to induce an expansion of the macrocycle. However it was observed that the rotation about $C\alpha$—$C\beta$ bond releases the steric strain during complex formation leading to hexanuclear metallamacrocycle.

The next step for the gradual increase of the nuclearity of the macrocycle by influencing the close contact interaction is introducing a single methyl substituent at the $C\alpha$ position. Presence of two methyl groups changes the close contact interaction from C_3 symmetry related $C\alpha$ methylene group to near neighboring N-acyl $C\beta$ methylene groups that falls on the same side of the macrocycle. This interaction leads to an expansion in the ring to an octanuclear system (Fig. 6) [78,79]. A further addition of a methyl group at one of the β positions expands the macrocycle to a decanuclear system by $C\beta$—$C\beta$ and $C\gamma$—$C\gamma$ methylene group interactions. The presence of three methyl groups at $C\alpha$ carbon of the N-acyl tail also yields a decanuclear system by
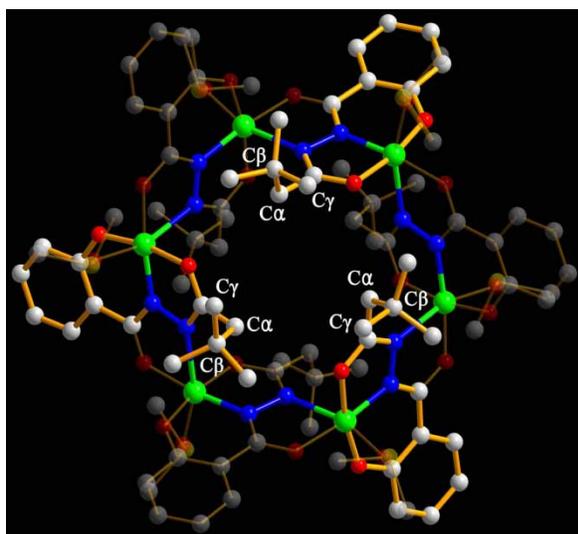

FIGURE 5 Ball and stick representation of a hexanuclear metallamacrocycle showing the close contact interaction between C_3 symmetric positioned N-acyl tail groups (see online for colour).
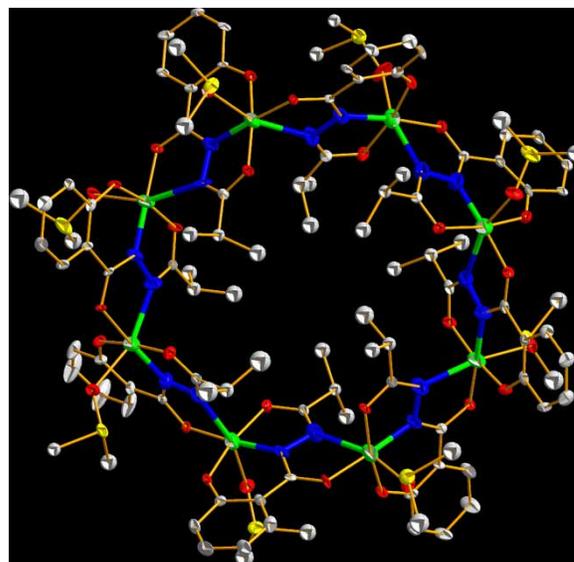

FIGURE 6 ORTEP diagram of an octanuclear metallamacrocycle prepared using a ligand with sterically least demanding two $C\beta$ carbon atoms as terminal N-acyl group. The 24-membered, 8-metal ring system is highlighted with thickened bonds, where the metal ions are presented in green and the bridging nitrogen atoms in blue (see online for colour).
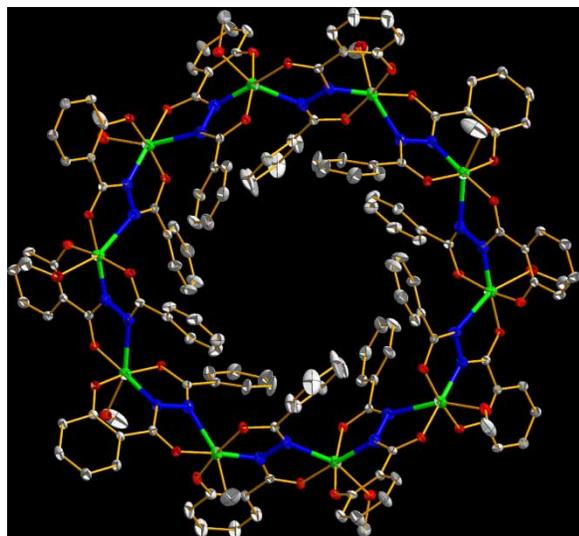
FIGURE 7   ORTEP diagram of a decanuclear metallamacrocycle with phenyl group as the *N*-terminal group. The 30-membered, 10-metal ring system was highlighted with thickened bonds, where the metal ions were presented in green and bridging nitrogen atoms in blue (see online for colour).
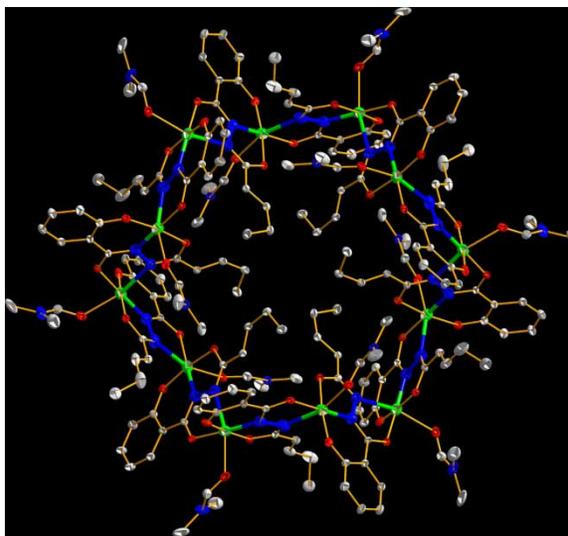

FIGURE 8   ORTEP diagram of a puckered dodecanuclear metallamacrocycle with $\ldots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\ldots$ chiral sequence. The 36-membered, 12-metal ring system was highlighted with thickened bonds, where the metals were presented in green and bridging nitrogen atoms in blue (see online for colour).

virtue of Cβ—Cβ close contact interactions [78]. The resulting decanuclear systems measure ~2.6 nm in diameter and ~1.2 nm in thickness. Introduction of a benzene at the *N*-acyl terminal where the substituent can be regarded as having geometrically fixed two β carbons two γ carbons and one δ carbon still yields a decanuclear system with manganese or iron rather than a macrocycle with higher nuclearity (Fig. 7) [80]. The magnitude of the steric interaction is the same as the closest approach is between Cβ atoms of the near neighboring *N*-phenyl units. The disc like molecule offers a cavity with an entrance diameter ~6 Å and ~13 Å at the interior which may serve as potential molecular recognition site. However no such recognition is yet reported by this macrocycle. Based on our observation we hypothesized that introduction of a double bond at Cα position may hinder freedom of rotation about Cα—Cβ bond and the lack of freedom of rotation would offer a directional option for the *N*-acyl tail but with limited steric crowding. One such group with Cα—Cβ double bond that could offer minimum steric crowding is the one having a *trans* methyl at Cβ. This modification yields an octanuclear macrocycle, with manganese as connecting node where the close contact interaction is between Cγ methyl and olefinic Cβ [81]. A further addition of methyl group at Cγ to the Cα—Cβ olefinic tail in the ligand unit yields a puckered dodecancuclear system with manganese when the crystals were grown from dmf (Fig. 8) [67,68]. This dodecanuclear macrocycle has a different configuration about the metal center in that the successive metal centers are in a $\ldots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\ldots$ chiral sequence compared to that of the rest of the compounds which varies as

$\ldots(\Lambda\Delta)(\Lambda\Delta)\ldots$. The former type of chiral sequence is due to the puckered ring conformation of S_6 symmetry [67,68]. The puckering is assumed to reduce the steric crowding of the rigid rod-shaped *N*-acyl tails at the core. The dodecanuclear metalladiazamacrocycle has six *N*-acyl tails directed to the interior of the core whose Cγ methylene groups are involved in close contact interaction, while the rest six tails away from the inner core of the macrocycle to avoid the steric crowding. The orientation of the rigid rod-shaped *N*-terminal groups leaves no meaningful cavity at the macrocyclic core.

Replacement of the *trans* methyl group at Cβ by a bulkier phenyl group (3-phenyl-*trans*-2-propenoyl group) in the salicylhydrazide ligand with manganese led to an icosanuclear metalladiazamacrocycle with a less regular $\ldots(\Lambda\Lambda\Delta\Delta\Lambda\Delta\Delta\Lambda\Lambda\Delta)\ldots$ chiral sequence (Fig. 9) [82]. This sequence leads the macrocycle to a 'cradle' like conformation of S_4 symmetry. The structural feature of this compound shows that unlike other macrocycles of the series four out of twenty ligands are in the 'inverted' conformation, where the sterically less demanding salicyl 'head domain' of the ligand rather than the sterically more demanding cinnamoyl (3-phenyl-*trans*-2-propenoyl) 'tail domain' is located at the inner core of the macrocycle. This unique conformation could be a result of the tendency of the system to reduce the steric repulsion at the core and provide a more thermodynamically stable conformation. By adopting an inverted conformation the macrocycle reduces the steric volume at the core. The relatively smaller size of the salicyl 'head part' decreases the steric repulsion at the core.
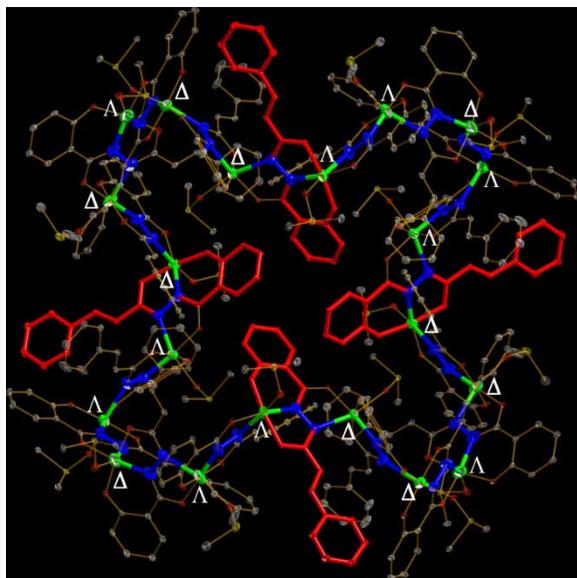
FIGURE 9 ORTEP diagram of an icosanuclear metallamacrocycle with ...(ΛΛΔΛΛΔΛΛΔΔ)... chiral sequence. The 60-membered, 20-metal ring system was highlighted with thickened bonds, where the metals were presented in green and bridging nitrogen atoms in blue. Four out of twenty ligands are in rather unusual 'inverted' conformation, where the phenyl 'head domain' of the ligand is located around the inner core of the macrocycle to reduce the steric repulsion (see online for colour).

Magnetic Properties of Metallamacrocycles

The magnetic properties of the manganese and iron complexes were investigated due to the M–N–N–M bridging present in the system. Most of the manganese complexes with high spin d^4 configuration show weak antiferromagnetic interactions with J values in the range of $-1.0\,\mathrm{K}$ to $-2.3\,\mathrm{K}$ [78]. In the case of corresponding iron(III) analogues with $S = 5/2$, only one octanuclear metalladiazamacrocycle was analyzed for magnetic property. This iron complex, like manganese complexes, shows antiferromagnetic interaction with J_1 and J_2 values in the range $-3.93\,\mathrm{cm}^{-1}$ and $-2.16\,\mathrm{cm}^{-1}$ respectively [79]. These weak antiferromagnetic coupling interactions could be due to the angle— > 90°—each diaza bridge subtends between the metal centers. A series of the macrocycles with systematically controlled nuclearities might provide the ideal model system for the detailed magnetic study of the weak antiferromagnetically coupled cyclic structures.

Recognition by a Metallamacrocyclic Host

While molecular recognition is an area of extensive investigation, several organic or metal-organic systems serve as host systems for a variety of molecules. The nature of the host cavity such as its shape and the functionalities plays a major role in choosing the guest it can accommodate. Fujita *et al.* have shown that metal-organic host systems with open portals prepared from the rigid aromatic ligands and *cis*-capped palladium metal ions can effectively encapsulate and retain hydrophobic guest molecules from a hydrophilic solvent system [8,9,41]. The various facial ligands were connected via palladium metal ions at the edges [6,83–85] or the corners [86–89] of the polyhedra to form metal-organic hosts with 3-D cavities. Raymond *et al.* have also prepared various metal-organic hosts with 3-D cavities based on the octahedral metal ions at the corners and the ditopic ligands at the edges of the polyhedra [23,90,91]. While the process of accommodation of a guest by these hosts depends on the competing forces of interaction between solvation, and encapsulation, the factor that favors encapsulation depends on the ability of host to involve the guest molecule in a variety of weak interactions such as hydrogen bonding, π–π, CH–π, dipole–dipole, and van der Waals interactions. Most of the literatures report recognition of small and large molecules by 3-D cavities [8–13]. The extent of molecular recognition by 2-D hosts like metallamacrocycles is few. This might be due to the limited efficiency of the metallamacrocycles with 2-D cavities for the recognition and selection of the guest molecules. However, a metalladiazamacrocycle can provide pseudo 3-D cavity because the disc-like macrocycle of thickness of ∼1 nm can generate a barrel-shaped cavity at the core even though the macrocycle itself is regarded as a 2-D species. The ability to recognize the hydrophilic or hydrophobic species by the metalladiazamacrocycle can be modified and controlled by changing the nature of the N-acyl tail. The hexanuclear cobalt metalladiazamacrocycle with the N-terminal amino groups in the cavity recognizes methanol molecules by virtue of the hydrogen bonding in addition to the size recognition [72]. Likewise it is possible to modify or affect the recognition properties of the metalladiazamacrocycle by using suitably designed hydrophobic N-terminal group. In our recent report the dodecanucler macrocycle with cyclohexyl N-terminal group can in fact recognize small hydrophobic molecules such as cyclohexane and cyclooctane using its pseudo 3-D hydrophobic cavity [92]. Use of a cyclohexyl group at the N-acyl position of the salicylhydrazide ligand introduces limited freedom of movement of the tail and the presence of two β, two γ and one δ methylene groups introduces an overall increase in steric volume. The presence of two β carbons and two γ carbons excludes the option of puckering of the ring leading to the formation of a dodecanuclear macrocycle with ...(ΛΔ)(ΛΔ)... chiral sequence. This leads the metallamacrocycle to S_{12} symmetry conformation, with an S_{12} symmetry hydrophobic pseudo 3-D cavity. The cavity has shown selectivity for guest molecules based not only on the size but also the symmetry. While a size matched cyclohexane could be accommodated into
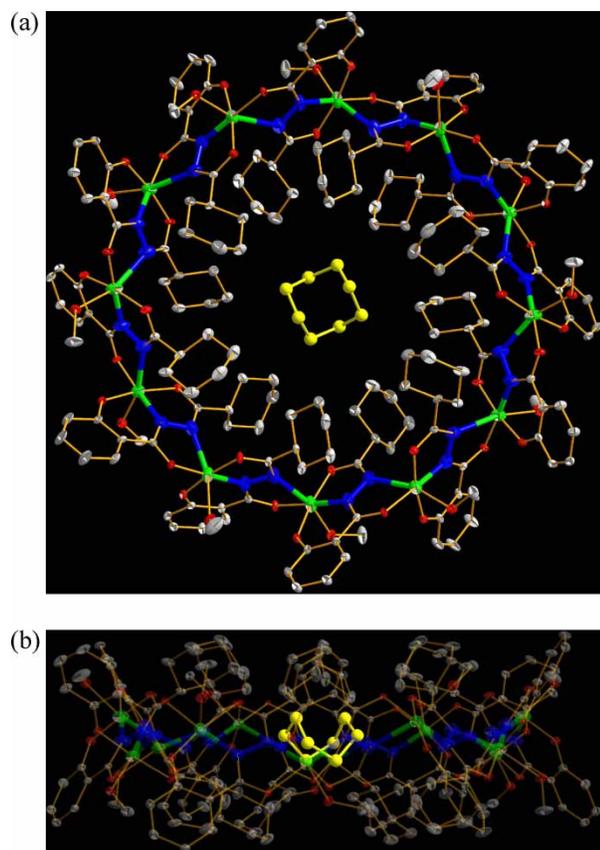
(a)

(b)

FIGURE 10 ORTEP diagrams of a dodecanuclear metallamacrocycle with ...$(\Lambda\Delta)(\Lambda\Delta)$... chiral sequence. A cyclooctane guest molecule is induced-fit into the S_{12} symmetry cavity of the macrocycle in a strained S_4 conformation rather than in a relaxed S_8 conformation. (a) Top view. (b) Side view.

the cavity, there were no evidence of the encapsulation of a size mismatched benzene guest molecule. More interestingly symmetry (or shape) mismatched guest molecule could be induced to fit into the cavity in a strained but symmetry matched conformation (Fig. 10). A cyclooctane guest molecule could be accommodated in the cavity in a strained S_4 symmetry conformation rather than in a relaxed S_8 symmetry conformation, since the S_4 symmetry is the subgroup of the cavity symmetry, S_{12}, while S_8 is not. This kind of induced-fit may provide the opportunity for the substrate activation in catalysis.

METALLADIAZAMACROCYCLES AS SUPRAMOLECULAR BUILDING BLOCKS FOR METAL-ORGANIC FRAMEWORKS

One of the main strategy for the construction of metal organic frameworks concerns self-assembly of the appropriate metal salts and a tailored ligand in a suitable solvent. Depending on the intrinsic properties of the metal ions and the ligands used, either supramolecular species or coordination networks [4–7] could be assembled. Even though controlling

or tuning the structures and properties of the supramolecular species were achieved to some extent, the ability to control the metal-organic frameworks with desired structures and properties is still a challenging goal. The small modification of the ligands and/or the replacement of the metal ions to control the metal-organic frameworks lead to completely unexpected new structures rather than isomorphic structures with tuned properties. One way to achieve this goal is the utilization of stable supramolecular building blocks [93]. The self-assembled metallamacrocycles using metal ions and bridging ligands can not only be used as supramolecular host systems for small guest molecules but also as supramolecular building blocks for the generation of various and/or tuned coordination networks. The metalladiazamacrocycles could be used as supramolecular building block because they have several replaceable solvent sites that can provide connection points between different building blocks [94]. Depending on their nuclearity, the macrocycles can be used as multitopic nodes for the metal-organic frameworks. The advantages of using these building blocks are: (1) it is possible to control systematically the nuclearity/shape of the building blocks by the introduction of various *N*-acyl tails without any significant perturbation of the structural and chemical features of the original building blocks; (2) this might lead to the systematic and controlled variations of the resulting architectures.

Various coordination networks could be prepared in one pot reaction using manganese acetate and trianionic pentadentate ligand, xshz^{3-}, for the construction of the supramolecular building block - the hexanuclear metalladiazamacrocycle, and 1,2-bis(pyridyl)ethane (bpea) as a linker ligand between the potential hexatopic building blocks. In the absence of bpea linker, the products are always metallamacrocycles of various nuclearities depending the ligands and metal ions used. When the ligands with linear flexible *N*-acyl tails were used, the potential trianionic pentadentate ligand, H$_3$xshz, bridges the metal ions to form an 18-membered hexanuclear metallamacrocycle as described in the section of the 'metalladiazamacrocycles'. Each metal center in the hexanuclear manganese metallamacrocycles is coordinated by five donor atoms from two chelating pentadentate ligands and an additional donor atom from a solvent molecule. When the metallamacrocycle is represented as a cyclic system with metal ions at the nodal points, the macrocycle seems to assume a cyclohexane-like backbone in chair conformation with replaceable solvents at the axial positions (Fig. 11). Three solvent molecules coordinated at the metal centers are in one face of the cluster, and the other three solvent molecules coordinated at the other metal centers are in the other face of the cluster. Thus the metallamacrocycles
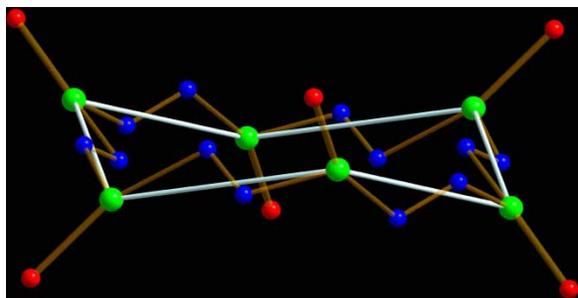
FIGURE 11 The core of a hexanuclear metalladiazamacrocycle emphasizing the hexatopic nature as a supramolecular building block, where the metals were presented in green, the bridging nitrogens in blue, and the solvents ligated to the metal ions in red. The ring metal ions in the cyclohexane-like chair conformation with the replaceable solvents can serve as the potential triangular nodes in the metal-organic frameworks.

with six replaceable solvent molecules could be used for the potential hexatopic supramolecular building

blocks to construct various three-dimensional coordination networks.

When the ligands with short and medium length linear and flexible N-acyl tail groups were used, exo-bidentate bpea ligand links the hexanuclear manganese metallamacrocycles to form three-fold interpenetrating 3-D network structures (Fig. 12) [95,96]. Only four out of the six potential solvent sites were replaced by the ditopic linker ligands which connect each hexanuclear manganese metallamacrocycle via 4_1 and 4_3 screw symmetry relationship. This type of the connectivity leads to three-fold interpenetrating 3-D network structures with nano-sized cavity, where two different types of 1-D channels parallel to the crystallographic c-axis were interconnected to form the 3-D cavity. Fig. 12b shows the connectivity of the metal ions in the three-fold interpenetrating 3-D net structure. Four out of six metal centers of the metallamacrocycle served as
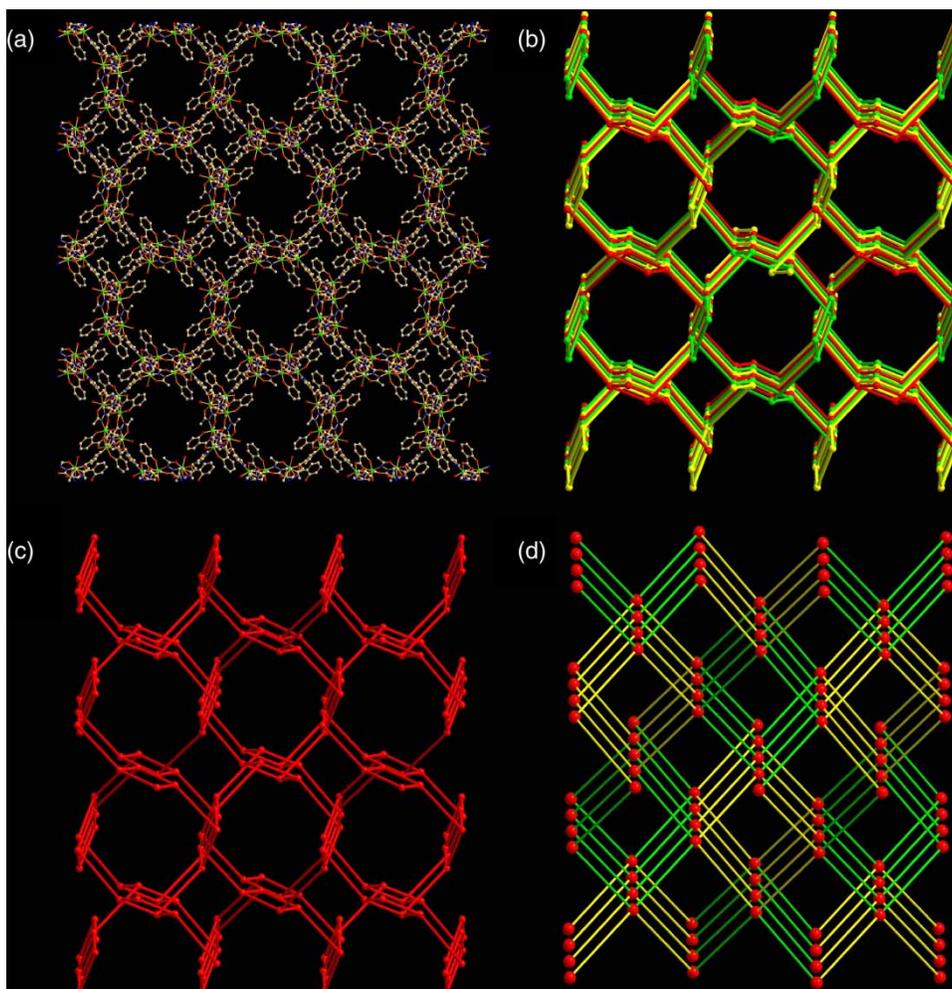

FIGURE 12 Three-fold interpenetrating 3-D network prepared using the hexanuclear manganese metalladiazamacrocycle as a supramolecular tetratopic building block related via 4_1 and 4_3 screw symmetry. (a) The packing diagram of the network shows two different types of channels along the crystallographic c-axis that linked each other to form 3-D cavities. Depending on the length of the N-acyl tails, the size and dimensionality of the cavity could be tuned. (b) The schematic drawing of the metal ion connectivity shows three interpenetrated 3-D nets represented in red, yellow, and green lines. (c) The individual net could be described as 3-connected 4.8.16 net, where only four metal ions of the macrocycle have served as 3-connectivity vertices. (d) When the metallamacrocycle presented as a rectangle was further reduced to a square node, the net described in (c) could be simplified to 4-connected $4^2.8^4$ net.

3-connectivity vertices. The individual net could be described as 3-connected 4.8.16 net (Fig. 12c). When the hexanuclear macrocyclic units were reduced to rectangular 4-connected vertices, the net could be further simplified to 4-connected $4^2.8^4$ net (Fig. 12d). Though the zeolite THO net has the same short Schläfli vertex symbol, the long symbol of the above mentioned net, $4.4.8_4.8_4.8_8.8_8$ [93,97], is different from that of THO's long symbol, $4.4.8_4.8_4.8_4.8_4$ [98].

The variation in tail lengths of the ligands does not affect the network structure, but the size and the dimensionality of the cavity could be tuned and controlled. As expected, the ligand with the shortest tail results in the network structure of the largest 3-D cavity, where only 51% of the whole crystal volume is occupied by the framework [95]. While the small increase in the tail length leads to the same type of network but with the reduced cavity size, the ligand with medium tail length again leads to the same network but with a change in the dimensionality of the cavity from 3-D to 1-D in addition to the reduced cavity size. The network structures with controlled cavity size and shape can be utilized for the size and shape recognition of the guest molecules. The networks with 3-D cavity can accommodate guest molecules with short alkyl pods such as methyl benzoate, ethyl benzoate, and isobutyrophenone as monopodal guests, and such as dimethyl phthalate

and diethyl phthalate as dipodal guests. The guest molecules with long pods such as propyl benzoate, butyl benzoate, dipropyl phthalate and dibutyl phthalate could not be accommodated regardless of their podality. The networks with 1-D cavity can only accommodate the guest molecules of mono-podality. The tuned isostructural networks with varying cavity size and shape could be constructed using a series of metalladiazamacrocycles of different size as supramolecular building blocks and showed the size and the shape selectivity for the guest molecules.

When the ligand with long and flexible *N*-acyl tail such as H_3lshz was employed for the preparation of the coordination network structure in a similar reaction condition, two mixed products were obtained in a single batch. One form of the network was isostructural with that described above and this network only had several small non-linked cavities. The other network structure had a different topology. The hexanuclear manganese metallamacrocycles were linked via the exo-bidentate bpea ligand to form two-fold interpenetrating 3-D network structure (Fig. 13) [96]. Even though only four among six solvent sites were replaced by bpea as in the previous network, the metallamacrocycles were connected via 3_1 and 3_2 screw symmetry instead of 4_1 and 4_3 screw symmetry. This connection mode
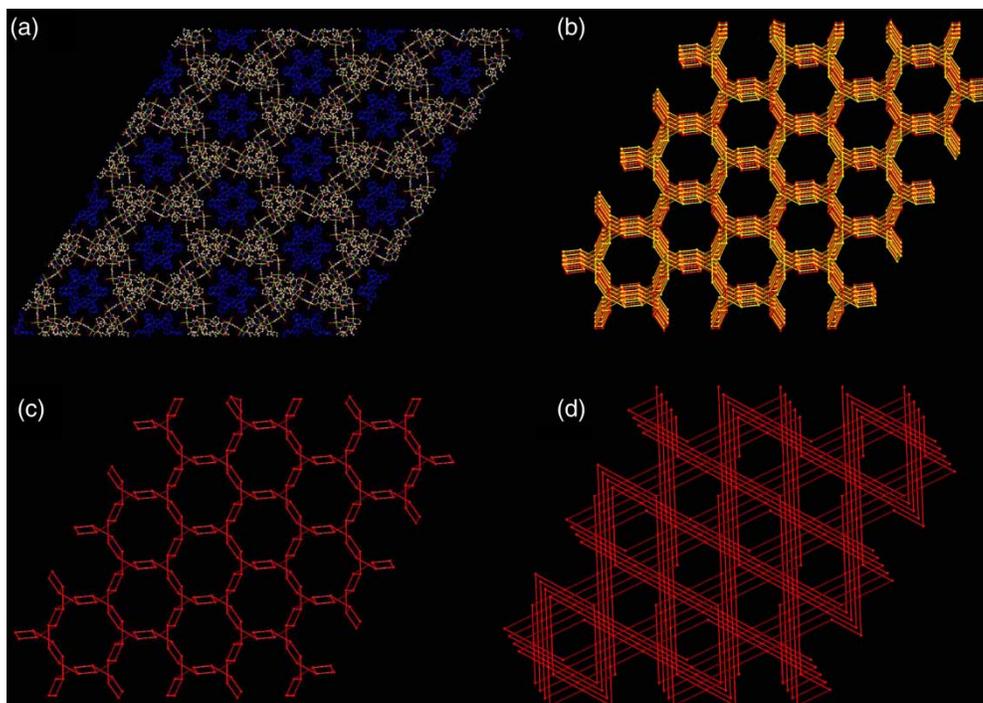

FIGURE 13 Two-fold interpenetrating 3-D network prepared using the hexanuclear manganese metalladiazamacrocycle as a supramolecular tetratopic building block related via 3_1 and 3_2 screw symmetry. (a) The packing diagram of the network shows 1-D channels along the crystallographic *c*-axis, where the metallamacrocyles (in blue) unconnected to the framework were stacked to fill the channel cavity. (b) The schematic drawing of the metal ion connectivity shows the two interpenetrated 3-D nets in red and yellow lines. (c) The representation showing the individual net as a 3-connected 4.12_2 net, where again only four metal ions of the hexanuclear macrocycle serve as 3-connectivity vertices. (d) Diagramatic representation of the simplified 4-connected $6^4.8^2$ net, when the metallamacrocycle presented as a rectangle in (c) was further reduced to a square node.
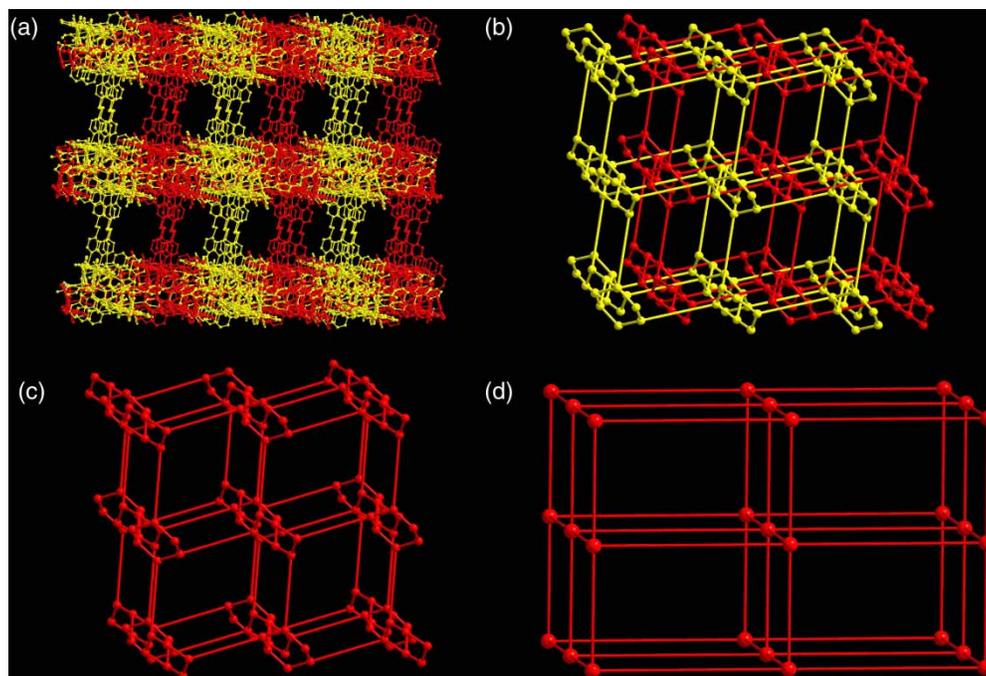
FIGURE 14 Two-fold interpenetrating 3-D network prepared using the hexanuclear manganese metalladiazamacrocycle as a supramolecular hexatopic building block. (a) The packing diagram of the network shows two interpenetrated 3-D nets in red and yellow, where one type of bpea linkers serve as pillars between the interwoven 2-D layers. (b) The schematic drawing of the metal ion connectivity shows the two interpenetrated 3-D nets in red and yellow lines. (c) The diagramatic representation of the net as a 3-connected 4.12_2 net, where all six metal ions of the hexanuclear macrocycle serve as 3-connectivity vertices. (d) The diagrammatic representation of the net as a well known simplified 6-connected simple cubic net, when the metallamacrocycle in the net described in (c) was further reduced to a simple octahedral node (colour in online version).

results in the 1-D channeled cavity of ∼2 nm in diameter along the crystallographic c-axis, and the cavities were stacked with unconnected metallamacrocyles leaving no additional void space for other guest molecules. The individual net in this structure could be described as another type of 3-connected 4.12_2 net (Fig. 13c). When the hexanuclear macrocyclic units were again reduced to rectangular 4-connected vertices, the net could be further simplified to 4-connected $6^4.8^2$ net (Fig. 13d). Even though this short vertex symbol is the same as that of NbO net, the long symbol, $6_2.6_2.6_2.6_2.8_6.8_6$, is different from that of NbO net, $6_2.6_2.6_2.6_2.8_2.8_2$ [99,100]. Both nets constructed using the metalladiazamacrocycle as supramolecular building block, are unprecedented even in the simplified forms, and this may be due to the use of metalladiazamacrocycle as a structurally rare rectangular 4-connected motif.

When the reaction was performed with H_3hshz having the medium length N-acyl tail in a similar condition but in the presence of potential guest and/or templating molecules, diethylphthalate, two different mixed crystalline products were obtained. The major product has the same net structure described as 3-connected 4.8.16 net and the minor product was confirmed as a different form of net. All six solvent sites of the hexanuclear metallamacrocycle were replaced by the exobidentate ligand bpea to provide a completely different type of two-fold

interpenetrating 3-D net (Fig. 14) [101]. This net can be described as two-fold interpenetrating 3-connected $6 \cdot 10^2$ (long symbol: $6 \cdot 10_2 \cdot 10_2$) net. When the hexanuclear metalladiazamacrocycles were handled as pseudo-octahedral hexatopic nodes, the network structure simplifies as a two-fold interpenetrating simple cubic net (Fig. 14b). Alternatively this framework could be considered as interlinked layers via bpea as shown in the Fig. 14a, where each layer was made from two interwoven 2-D nets. The interaction within each layer is through the hydrophobic contacts of the metalladiazamacrocyclic building blocks. The framework of this net was calculated to occupy about 49% of the crystal volume.

CONCLUSION

The metalladiazamacrocycles that contain metal ions and diaza groups as ring constituents can be prepared by facile self-assembly of tricationic octahedral metal ions and N-acylsalicylhydrazidates as pentadentate trianionic ligands. The ligand binds a metal ion in a chelating tridentate mode on one side and bidentate mode on the other. This binding mode is propagated through successive metal centers leading to various cyclic structures. The way of coordination of two chelating ligands around the metal center in a cyclic structure generates the metal

center of Λ or Δ chiral configuration depending on the direction of the chelating ligands. When the ligands with linear or β-substituted *N*-acyl tails were combined with various tricationic octahedral metal ions, isostructural 18-membered hexanuclear metal-ladiazamacrocycles were obtained regardless of the metal ions and the solvents used. The metal centers are in the alternating ...(ΛΔ)(ΛΔ)... chiral sequence and the three alternating *N*-acyl tails are oriented on one face while the other three on the other face of the disc-like macrocycles. The introduction of the ligands with sterically demanding *N*-acyl tails can expand the macrocyclic rings from hexanuclear up to icosanuclear systems. The ligand of the Cα sub-stituted *N*-acyl tail with the least steric volume leads to octanuclear metalladiazamacrocycles. Further increase in the steric volume of the Cα substituted *N*-acyl tail generates decanuclear and dodecanuclear metalladiazamacrocycles with the alternating ...(ΛΔ)(ΛΔ)... chiral sequence depending on the steric repulsions between the tail groups. The metallamacrocycles with regularly alternating ...(ΛΔ)(ΛΔ)... chiral sequence generate the pseudo 3-D cavity in the inner core. Depending on the nuclearity and environment of the core not only the size and symmetry of the cavity but also the functionality of the core could be modulated. Especially, the symmetry of the cavity can induce the encapsulated guest molecule to adopt a strained conformation. The modulation of the nuclearity of the metalladiazamacrocycles could be alternatively achieved by reducing the rotational degree of the freedom of the *N*-acyl tails. The ligands of *N*-acyl tails with double bond at Cα and Cβ where the tails behave like the rigid rod but provide relatively small steric volume can lead to macrocycles of higher nuclearity but more puckered conformations with less regular chiral sequences. The puckering might be caused to reduce the steric repulsion on one hand and on the other hand to maximize the van der Waals interactions around the core region, thus reducing cavity. However when the ligand with extended rigid tail such as 3-phenyl-*trans*-2-propenoyl group was used, some of the ligands adopt an 'inverted' conformation to reach a compromise between the excessive steric repulsion and the increased van der Waals contacts at the inner core.

The metalladiazamacrocyles could be used as supramolecular building blocks because they have several replaceable solvent sites that can be used as connecting nodes. The hexanuclear metalladiazama-crocycles with six replaceable solvent sites can serve as potential hexatopic node for the metal organic frameworks. The systematically tuned isostructural 3-fold interpenetrating 3-D nets with various cavities could be generated using a series of manganese hexanuclear metalladiazamacrocycles, where the macrocycles serve as rare rectangular tetratopic

nodes. Depending on the length of *N*-acyl tails, the size and the shape or dimensionality of the cavities could be controlled and these cavities can recognize the guest molecules based on size and shape preference. Either the further modification in the ligand, the primary building unit, or the change in the reaction condition such as presence of the templating molecules provide the different types of frameworks. The ligand with long linear *N*-acyl tail gives different network topology. Even though the metalladiazamacrocycles also serve as tetratopic node as in the previous net, the nodes were connected 3_1 and 3_2 screw symmetry rather than 4_1 and 4_3 screw symmetry. The presence of the shape mismatched guest molecules in a similar reaction condition leads to completely different type of net topology. The network is a two-fold interpenetrating simple cubic net, where the metalladiazamacrocycles served for the pseudo octahedral hexatopic nodes.

The appropriate design of the primary building units such as metal ions and multidentate ligands can lead to systematically modified supramolecular systems where the coordination bonds can substitute the multiple weak interactions for directing the primary building units for the organized structures. These species could serve not only for the supramolecular host systems but also be used as supramolecular building blocks for the construction of the various metal organic frameworks with tuned properties.

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