Review

Self-assembly directed by dinuclear zinc(II) macrocyclic species

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Contents

Abstract

Supramolecular compounds assembled by dinuclear zinc(II) species containing Robson-type macrocycles and diverse organic subunits (4,4′-bipyridine, 2,2′-bipyridine, pyrazine, 4-aminopyridine, 4-pyridinecarboxylate, pyridine, and quinoline) are reviewed. Various structural motifs such as molecular ladder, molecular ladder element and so forth have been generated. Structural attributes associated with each motif will be elucidated based on unambiguous single crystal X-ray analysis. Hydrogen bonding especially of the non-classical type, involved in the assembly are also discussed because of its crucial impact on the architecture of the final product.
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Keywords: Self-assembly; Coordination bond; Hydrogen bond; Dinuclear zinc(II); Macrocycle

1. Introduction

The supramolecular self-assembly process, which has been universally recognized to be crucial in the proliferation of all biological organisms, offers considerable advantages for development of novel functional molecular materials compared to that of conventional linear synthetic methodology [1]. So far, a variety of well-defined supramolecular arrays with diverse structural motifs have been realized based on the concept of self-assembly, which was driven by such non-covalent interactions as coordination bonding, hydrogen bonding, aromatic π–π stacking and so on. Among various assembling strategies, self-assembly of metal-containing building blocks via coordination bonds has been actively investigated in recent years and successfully employed in the formation of a wide range of functionally active supramolecular species [2]. Quite recently, mononuclear-containing macrocyclic complexes have emerged as versatile building blocks for supramolecular self-assembly exploration [3], among which metalloporphyrin-type complexes are presented as a typical example [4]. However, reports on self-assembly with dinuclear macrocyclic complexes still remain rare [5].

In this review, we will demonstrate the self-assembly directed by dinuclear zinc complexes of Robson-type macrocycles with particular emphasis on structural attributes of the resultant supramolecular complexes. Moreover, hydro-

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gen bonding, especially in a non-classical form, will also be discussed in a separate section considering its crucial impact on the architecture of the final products.

2. Dinuclear zinc(II) complexes of Robson-type macrocycles

Since the pioneering work of Pilkington and Robson [6], dinuclear macrocyclic complexes, owing to their special coordination ability, have been extensively studied as models of metallobiosites and appropriate systems of activating simple molecules [7]. Over the past years, much effort in our group has also been made into this exciting and growing area, and a series of dinuclear [8] and polynuclear complexes [9] of Robson-type macrocycles have been achieved by sodium-template reaction. Among these macrocyclic complexes, from the viewpoint of self-assembly, the dinuclear zinc(II) complexes (**1a** and **1b**) are of particular appeal. Their structures have been unambiguously elucidated by single crystal X-ray analysis [8c]. As shown in Fig. 1, two zinc(II) ions are located in the tetra-imine macrocyclic cavity, wherein each metal takes a distorted square pyramidal geometry with an apical position occupied by a water molecule. Two water molecules are situated above and below the macrocyclic platform to avoid steric repulsion. The two apical water molecules are only weakly coordinated rendering them readily displaced by other strongly ligating groups (e.g. azide and

halide anions). Thus there are at least two apical coordination sites to be utilized for further assembly. Furthermore, each zinc(II) ion is of a suitable size that it can move up and down out of the macrocyclic plane under some conditions. The short intermetallic separation (ca. 3.2 Å) restricts some aromatic compounds from adopting face-to-face stacking modes. As described above, each complex (**1a** or **1b**) possesses an ideal rigid macrocyclic platform and the zinc ions provide flexible coordination numbers (five or six). These intriguing features prompted us to explore self-assembly induced using these dinuclear complexes. Not all macrocyclic compounds are suitable candidates for the study of self-assembly. For instance, attempts to achieve self-assembly with dinuclear copper(II) species of the same macrocycle were unsuccessful in our previous trials. Only certain rigid macrocycles containing specific metals with appropriate size and flexible coordinating numbers could be selected for further assembly.

3. Self-assembly with linear homo-bifunctional organic ligands

Linear homo-bifunctional organic ligands, such as 4,4′-bipyridine, pyrazine and so on, are frequently used for the construction of diverse supramolecular architectures. In fact, the first example of self-assembly directed by dinuclear zinc(II) macrocyclic species was realized by 4,4′-bipyridine, generating an infinite 1D molecular ladder [10] (Fig. 2). 4,4′-
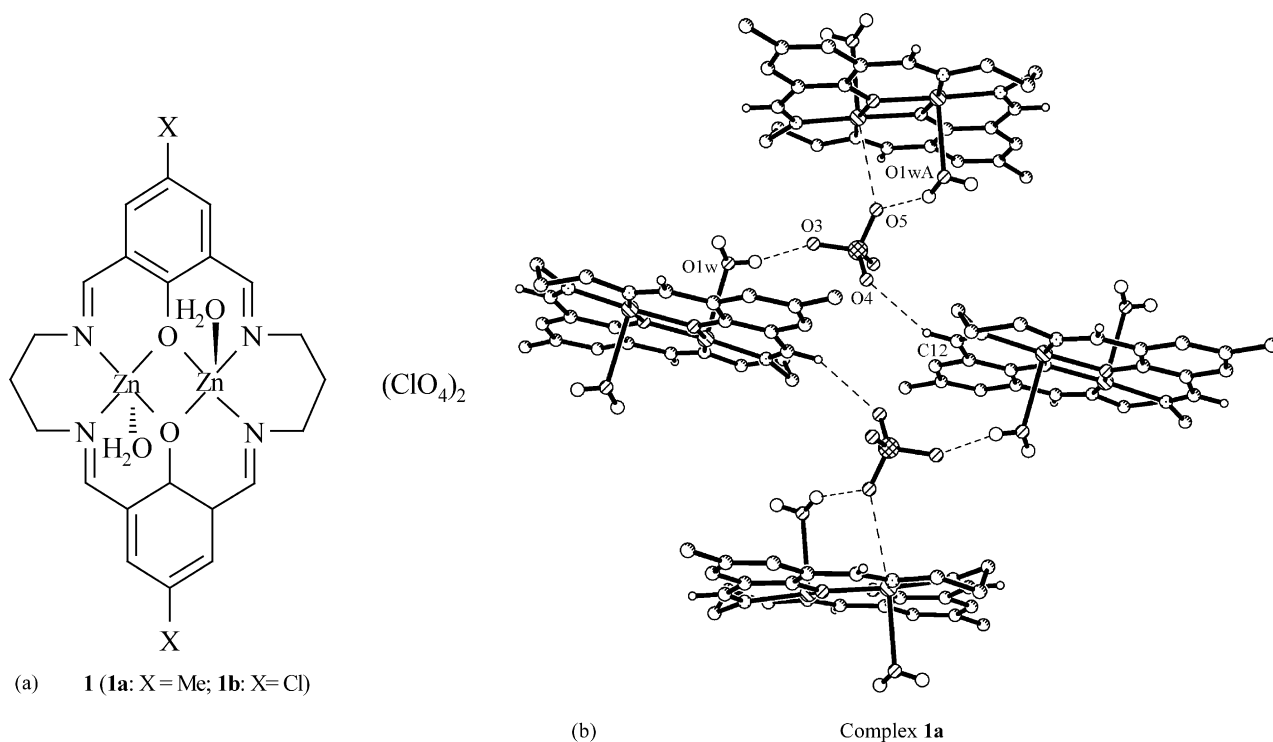

Fig. 1. (a) Dinuclear zinc(II) complexes of Robson-type macrocycles; (b) hydrogen bonding interactions in the crystal packing of **1a** where perchlorate anions act as bridges, hydrogen atoms not relevant to H-bonds are omitted for clarity.

$[Zn_2L(H_2O)_2](ClO_4)_2$

1a and 1b

+

4, 4'-bipyridine

$\xrightarrow[C_2H_5OH]{CH_3CN}$

(a)   2a and 2b
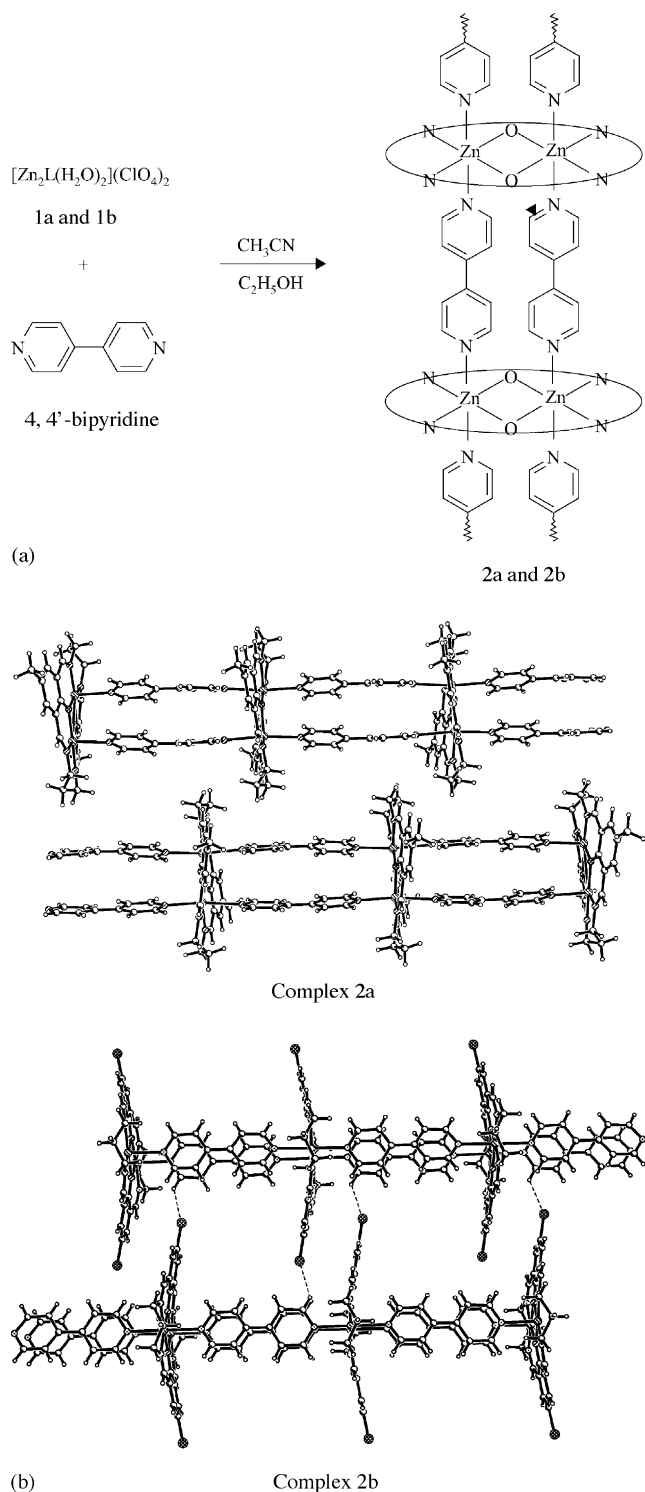

Complex 2a

(b)   Complex 2b

Fig. 2. (a) Self-assembly with 4,4'-bipyridine; (b) perspective views of packing structures of **2a** and **2b**.

Bipyridine serves as organic linker via coordination bonds, all perpendicular to the macrocyclic platform. The two pyridine rings of one 4,4'-bipyridine molecule are staggered with a dihedral angle of 6.3°, but are parallel with their counterparts. The 4,4'-bipyridine molecules connect the zinc

metal centers on the same side of the macrocyclic platform, contrary to the previous observation of opposite-side coordination modes for small mono-functional molecules such as water, azide and halide anions as well as tetracyanoquinodimethane [6,8b,11]. It is likely that the strength of the coordinative bonds and the π–π interactions between two close 4,4'-bipyridine molecules overcomes the spatial repulsion to preserve the molecular ladder motif. Similar face-to-face π–π stacking of 4-pyridyl rings has also been observed in the crystal structure of molecular rectangles assembled from the binuclear copper(II) moiety of a compartmental end-off ligand with 4,4'-bipyridine reported by Andruh and his co-workers [12]. As expected, rectangular hydrophobic cavities (3.150 Å × 11.750 Å) without any guest molecule were found in **2a**, wherein the 4,4'-bipyridine ligands connect the Zn(II) ions to serve as the "side rails" (long sides) and the phenolic oxygen atoms on the ring link the Zn(II) ions to act as the "rungs" (short sides). To the best of our knowledge, this is the first report on molecular ladders that have no interpenetrated network entangled or guest molecules clathrated in the ladder cavity. Similarly, a comparable molecular ladder motif was obtained by the assembly of 4,4'-bipyridine with **1b**. In contrast to **2a**, non-classical hydrogen bonding C–H···Cl was involved in the crystal stacking of **2b** due to the chlorine atom on the aromatic ring, to be discussed below.

Minor variations in organic building blocks have a profound effect on the architecture of the final supramolecular assembly. Astonishingly, reaction of 2,2'-bipyridine with the dinuclear zinc macrocyclic complex led, unexpectedly, to the formation of a supramolecular assembly lacking 2,2'-bipyridine, composed of a unique open-mouthed sandwich-like structure containing two macrocyclic covers bridged by two OH groups in the middle [13] (Fig. 3). Clearly, the 2,2'-bipyridine molecule functions as a base to assist hydrolysis at the zinc(II) cations, a Lewis acid under the conditions of the experiment. Most probably steric hindrance between the organic ligand and macrocyclic platform inhibited formation of an assembly containing 2,2'-bipyridine. In complexes **3a** and **3b**, all metal atoms have similar pyramidal configurations where each zinc(II) atom is situated slightly above the base plane composed of two imine nitrogen atoms and two phenolic oxygen atoms, with the axial position occupied by one OH group. Each macrocyclic framework is folded to fit the requirement of two Zn–OH–Zn bond angles [**3a**: 133.6(3)°, 137.8(3)°; **3b**: 133.3(3)°, 141.8(3)°]. In each subunit of one molecule, one part of one ring is nearly parallel to its counterpart in the other one (with a dihedral angle of 9.1° in **3a** and 0.2° in **3b**), while the other parts of the two rings are bent in the opposite position (with a dihedral angle of 42.8° in **3a** and 56.5° in **3b**). Each structure shows a rectangular Zn_4 array containing a rigid Zn_4O_4 cavity in both compounds. This arrangement is similar to that reported by Asato et al. in which a tetranuclear zinc(II) complex was synthesized by a template condensation [14]. The cavity is so small that neither solvent molecules nor perchlorate anions can be hosted. Compared with **3a**, non-classical hydrogen bonding partici-
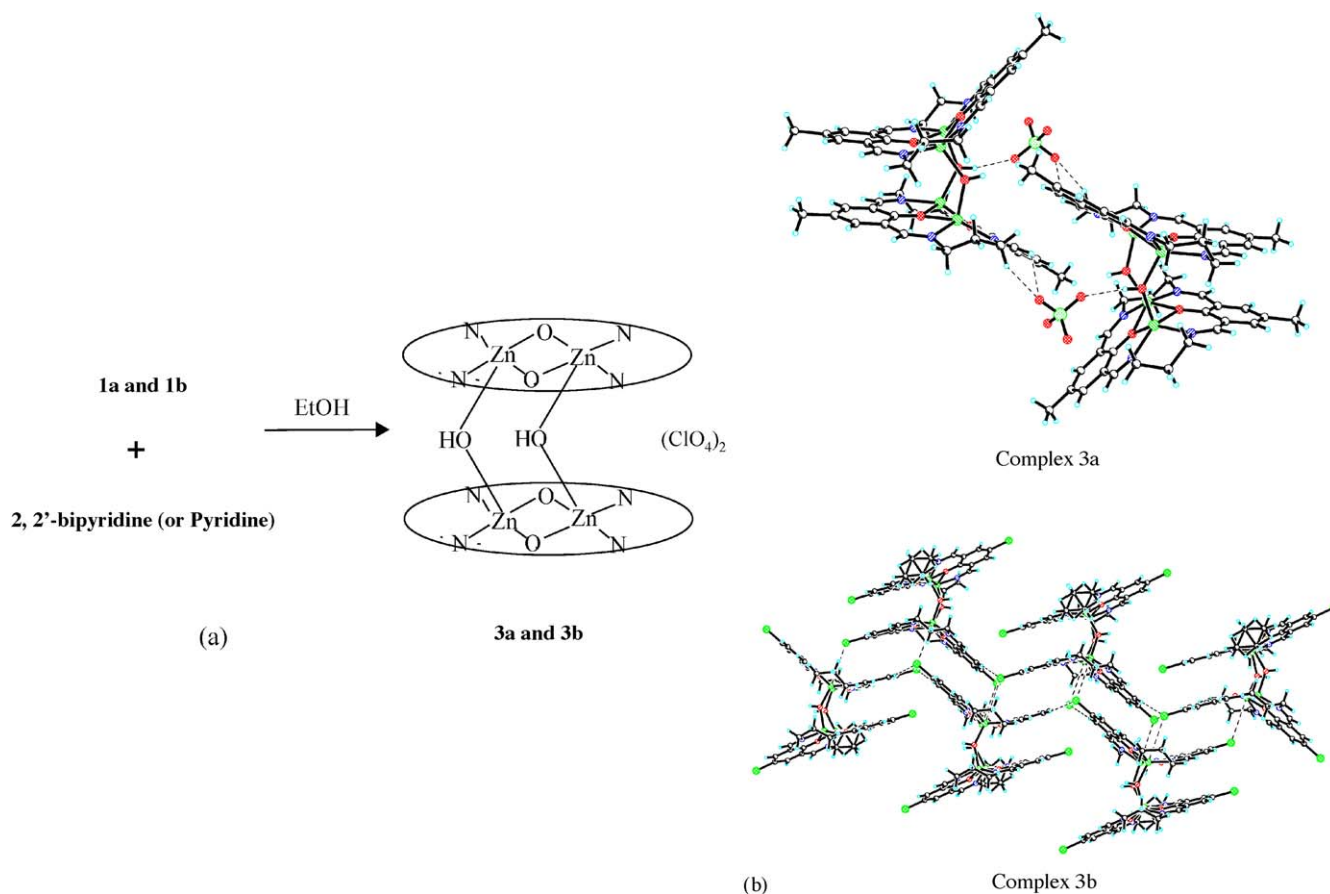
Fig. 3. (a) Self-assembly with 2,2′-bipyridine (or pyridine); (b) supramolecular interactions between vicinal molecules of **3a** (**3b**).

pates in the stacking process of **3b**, resulting in a dramatically different gross structure.

Pyrazine, another versatile linear bifunctional organic ligand, was also investigated. Irrespective of structural similarities between pyrazine and 4,4′-bipyridine, the analogous molecular ladder motif was not achieved as predicted. Contrary to our expectation, a new type of infinite chain polymers was produced, in which dinuclear zinc(II) macrocyclic platforms are bridged by formate anions in an end-to-end manner via coordinate bonding [15] (Fig. 4). The presence of formate anions in this assemblage is of interest considering that no starting material contains this species. In a contrasting experiment, treatment of dinuclear zinc(II) macrocyclic complexes with formic acid in the presence of sodium hydroxide produced solids whose microanalytical data are in good agreement with those of **4a** and **4b**. It is still unclear what the source of formate species is, but some clues may be found in the published work on metal-catalyzed (Cu, Zn, Co, Fe, Ru, etc.) hydrogenation of carbon dioxide to formic acid [16]. The formate anions in **4a** and **4b** may result from the Zn(II)-catalyzed reduction of carbon dioxide absorbed by the mother liquor during the formation of single crystals. Both **4a** and **4b** consist of a complex cation charge balanced by an independent perchlorate anion. In both compounds, two metal atoms are located in a square pyramid configuration as that in **1**. Donors on the macrocyclic framework offer a N_2O_2 base plane, but the axial position is displaced by one oxygen atom of a formate anion. Two formate anions are on the each side of macrocycle, connecting one zinc(II) atom, respectively. Compared with complex **1**, the related Zn–O bond lengths are shorter from 2.088 Å in **1** to 2.003 Å in **4a** and 1.998 Å in **4b**, respectively. Furthermore, each formate anion acts as a bidentate bridging ligand linking adjacent macrocyclic components to form an infinite coordination polymer. Unlike those with the rigid pyridine-based ligands, the adjacent macrocyclic units in **4** are not parallel to each other. They are situated at a dihedral angle of 58.5° (**4a**) and 51.9° (**4b**) to suit the geometric requirement of each metal atom and to minimize the spatial repulsion. The separations between the two zinc(II) ions linked by formate anions are 5.803 Å (**4a**) and 5.747 Å (**4b**), respectively. The above-mentioned structure is different from that of Manoharan group's report in which a dinuclear nickel(II) component of the same macrocyclic ligand is bridged by 1,3-diaminopropane and nickel atoms are placed in a distorted octahedral environment where the sixth position is taken by a water molecule [5b]. In addition, the same supramolecular array was obtained with an alkyl substituted pyrazine.

$[Zn_2L(H_2O)_2](ClO_4)_2$

1

+

(pyrazine structure)

EtOH →

$(ClO_4)_2$

(a)   R = H or CH₃
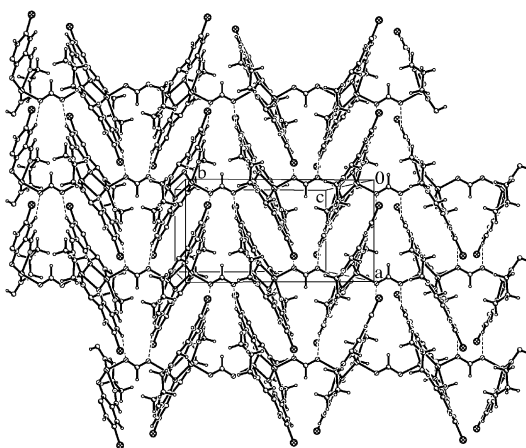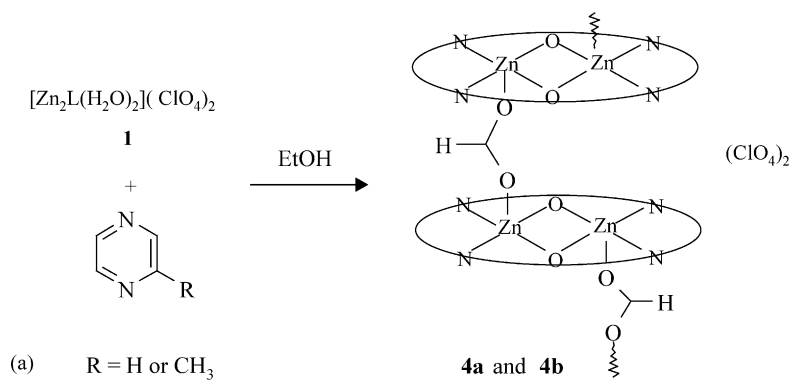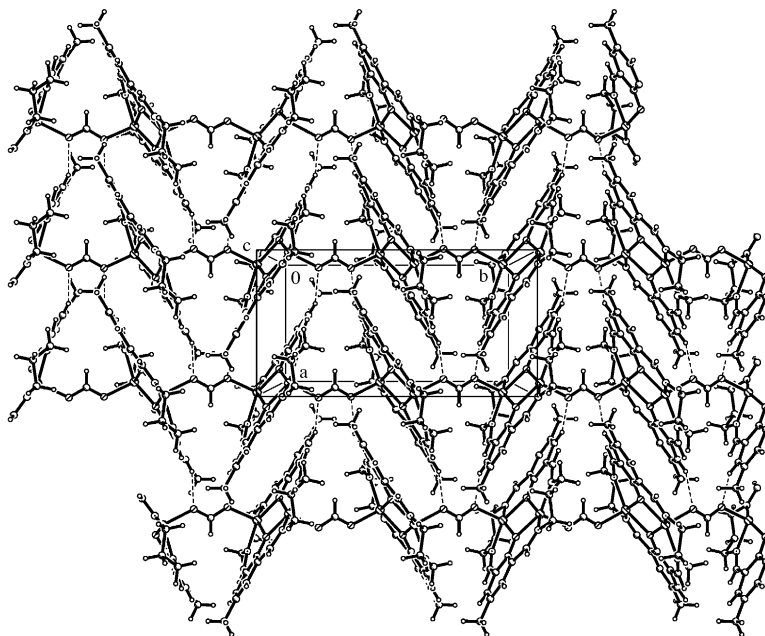
4a and **4b**

Complex **4a**

(b)   Complex **4b**

Fig. 4. (a) Self-assembly with pyrazine (or 2-methylpyrazine); (b) view of the 2D network depicting the connection via weak C—H···O hydrogen bonds in **4a** and **4b**.

4. Self-assembly with hetero-bifunctional organic ligands

Hetero-bifunctional organic ligands with two different coordination sites have also been used to examine self-assembly with the dinuclear zinc(II) macrocyclic complexes. Indeed, fascinating results have been gained with organic ligands of this category. Assembly of 4-aminopyridine with dinuclear zinc(II) macrocyclic compound **1a** produced a novel supramolecular array **5a** composed of molecular ladder elements with macrocyclic platforms [17] (Fig. 5). Each zinc(II) atom on the macrocyclic framework is bound to one 4-aminopyridine molecule, resulting in a pyramidal rather than an octahedral coordination environment around the metal atom. The axial position is occupied by the pyridine nitrogen atom due to its stronger coordination ability than that of the amino group and water molecule. However the amino group is uncoordinated and no ladder motifs were produced. Differing from the other known structures of five-coordinated zinc(II) complexes of this macrocyclic ligand, two pyridine rings are set in the same direction of the macrocycle which is slightly bent with an angle of N(2)−Zn(1)−Zn(2) in 93.5°. The two pyridine planes are oriented in a nearly parallel way via π−π interactions, forming a concavity structure. The distance between the two pyridine planes is ca. 3.5 Å, a bit longer than that of the two metal atoms. The most important feature is that a hydrogen-bond cycle has been formed, generated from hydrogen atoms of two amino groups with two perchlorate anions. Each ClO_4^- group acts as a bridge to link two amino species through N−H···O bonding, consisting of a 12-membered hole on top of pyridine rings. The hole with dimensions of ca. 3.77 Å × 7.29 Å is about 6.21 Å deep to the macrocyclic base. The existence of such a H-bond-formed cycle supports two 4-aminopyridine species to stand face to face through a weak molecular inter-action on the macrocyclic platform by one-end coordinate bonding.

In our molecular ladder motifs, dinuclear zinc(II) macrocyclic moieties play a key role in maintaining the ladder structure, because the coordination bonding between the metal atom and 4,4′-bipyridine is much stronger than the π−π interaction between the pyridine planes and overcomes the steric repulsion. But here hydrogen bonding plays a significant part in sustaining such an assembly of 4-aminopyridine molecules. The assembly of **1b** with the same organic ligand resulted in a different architecture in our previous trial. The rough single crystal data indicated that 4-aminopyridine units are in *trans*-configuration of the macrocyclic platform. Although we did not obtain high quality single crystal, it is obviously possible to regulate the orientation (*cis* or *trans*) of the organic subunits by controlling the reaction conditions.

Interestingly, assembly of **1a** with 4-pyCOO⁻ resulted in a wheel-like architecture with two substituted pyridine groups placed in a reverse position [17] (Fig. 6). Two zinc(II) atoms in a macrocyclic framework adopt a five-coordinate configuration analogous to that of **5a** except that one apical position is taken by one nitrogen atom and the other by one oxygen atom of 4-pyridinecarboxylate. Although 4-pyridinecarboxylate works as a linear bifunctional ligand in which the anion is monodentate, a 1D molecular ladder network similar to the case of 4,4′-bipyridine was not produced. However, an approximate parallelogram consisting of a tetranuclear zinc(II) unit was formed. Two pyridine rings are parallel to each other with a very short separation of ca. 3.2 Å via π−π interactions. The Zn−Zn distance in the macrocyclic subunit is 3.18 Å, and the parallelogram is ca. 8.99 Å × 3.18 Å in length with angles of 93.8° and 86.2°, respectively. The resultant cavity is so small that no guest species or molecules can be accommodated. The coordinated C−O unit is not coplanar to the attached pyridine plane,
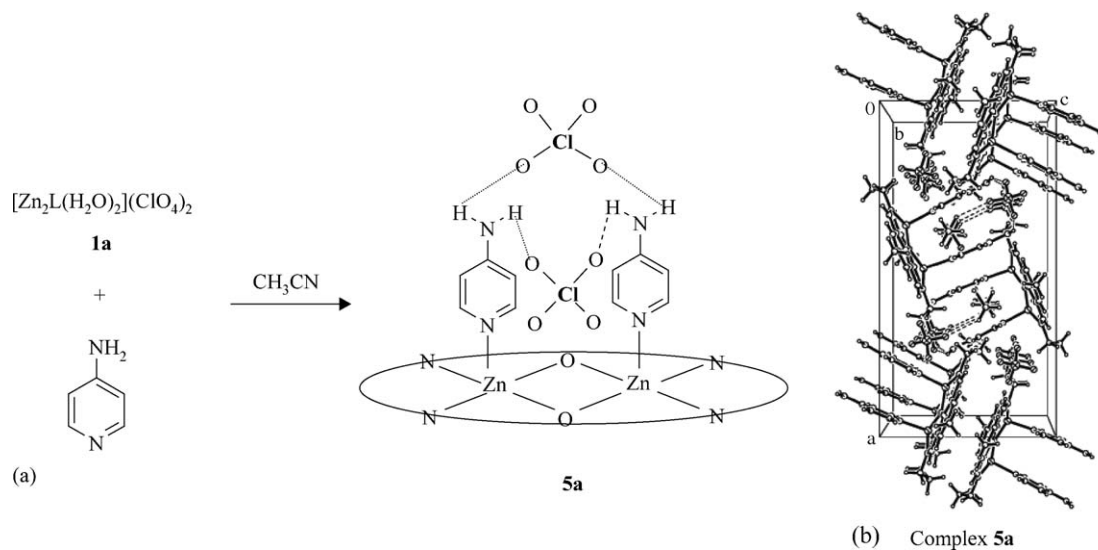

Fig. 5. (a) Self-assembly with 4-aminopyridine; (b) view of packing structure of **5a**.

(a)   6a

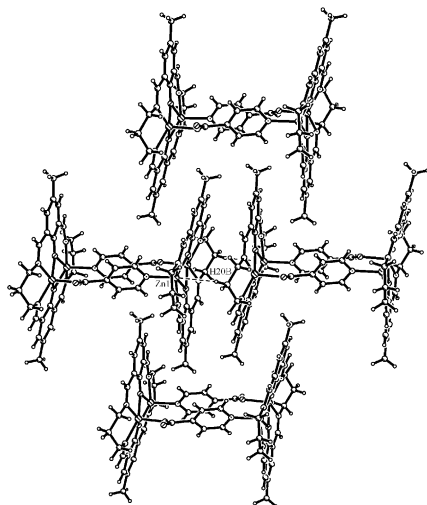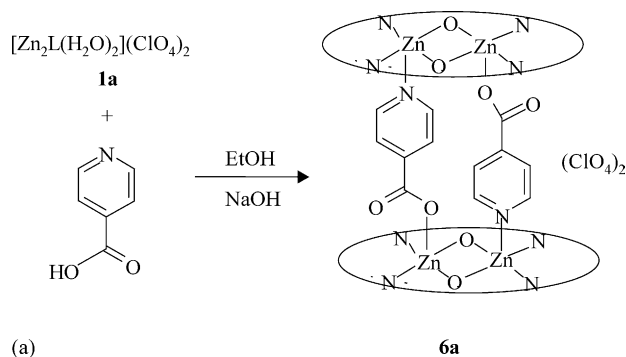(b)   Complex **6a**

Fig. 6. (a) Self-assembly with 4-pyridinecarboxylate; (b) view of packing structure of **6a**, the distance between Zn1 and H20B bonded to the middle carbon atom of 1,3-diaminopropane is 2.891 Å.

forming a torsion angle of ca. 40°. Such a twist provides the necessary space for the configuration deployment of four five-coordinated zinc(II) atoms.

5. Self-assembly with monofunctional organic ligands

Attempts were made to assemble monofunctional organic ligands with dinuclear zinc(II) macrocyclic subunits to obtain an in-depth appreciation of the nature of this assembling system. Self-assembly with pyridine led to the formation of the same supramolecular assembly as was the case with 2,2′-bipyridine, an open-mouthed sandwich-like structure consisting of two macrocyclic covers with two bridging OH groups in the middle [13] (Fig. 3). The lack of the pyridine molecule in the final product may result from the free rotation of the single Zn–N(pyridine) bonds which makes it impossible to attach to the macrocycle due to the spatial repulsion. Consequently, the monofunctional aromatic ligands cannot displace the 4,4′-bipyridine ligands, which are framed with the assistance of the macrocyclic skeleton.

However, assembly with 2-methylquinoline resulted in an infinite 1D hydrogen-bond-supported donor–acceptor polymer, dramatically different from the reaction with pyridine, wherein no coordinating interaction occurs between layers [13] (Fig. 7). The two nitrogen atoms from 2-methylquinoline molecules are linked to two coordinating water molecules above and below the macrocyclic framework through hydrogen bonds. Two hydrogen-bonded quinoline rings are found in an almost parallel position to the phenyl ring in the macrocyclic plane (with a dihedral angle of 6.3°). Moreover, they lie in a face-to-face fashion with the adjacent macrocyclic frameworks on their other side. Two quinoline rings, situated between two macrocycles are strictly coplanar each other forming an ordered arrangement where one macrocycle and two 2-methylquinolines are alternatively arrayed. The separation between the macrocycle and quinoline rings is about 3.6 Å, indicating that aromatic π–π interactions are present between quinoline and phenyl species in the macrocyclic skeleton, where the electron-rich quinoline moiety (uncoordinated) acts as a donor and the electron-poor phenyl species (owing to the coordination of the macrocyclic ligand) act as acceptor. It is suggested that both the π–π interaction and the H-bonding interaction dominate such a stacking structure. Displacement of 2-methylquinoline with 8-methylquinoline yielded a layer-like structure (**7b**) similar to **7a** [18].

6. Hydrogen bonding involved in the self-assembly

Although self-assembly directed by dinuclear zinc macrocyclic species was mainly assisted by coordination bond-based approach, other non-covalent interactions such as aromatic π–π stack and hydrogen bonding also have a significant impact on the architecture of the final product. In our assemblies, various hydrogen-bond patterns including non-classical versions participate in the crystal stacking process, producing versatile supramolecular motifs.

In the 4,4′-bipyridine example, adjacent ladders of **2b** were linked by C–H···Cl hydrogen bonding to give a 2D network, which was markedly different from those of **2a** without any connection (Fig. 2(b)). Weak non-classical hydrogen bonding of such a type in **2b** arises from the intermolecular interaction between the top chlorine atom of one macrocyclic framework of one ladder and the hydrogen atom attached to a pyridine ring of the neighboring ladder. The geometric dimension of the H-bonding here is 2.898 Å in length and 133.8° in angle. In addition, C–H···O bonding has also been observed in the crystal structures of both compounds **2a** and **2b**. In **2a**, there are three types of hydrogen bonds (2.554 Å, 129.01°; 2.593 Å, 141.43°; and 2.591 Å, 132.34°) where the H-bonding acceptor is from one oxygen atom of the perchlorate anions. But the related H-bonding donor comes from different sources, the first two from one carbon atom of the 1,3-propanediamine group of the macrocyclic framework and the last from a pyridine unit. In **2b**, such C–H···O bonds are 2.564 Å, 156.50° and 2.592 Å, 132.15°, respectively. The
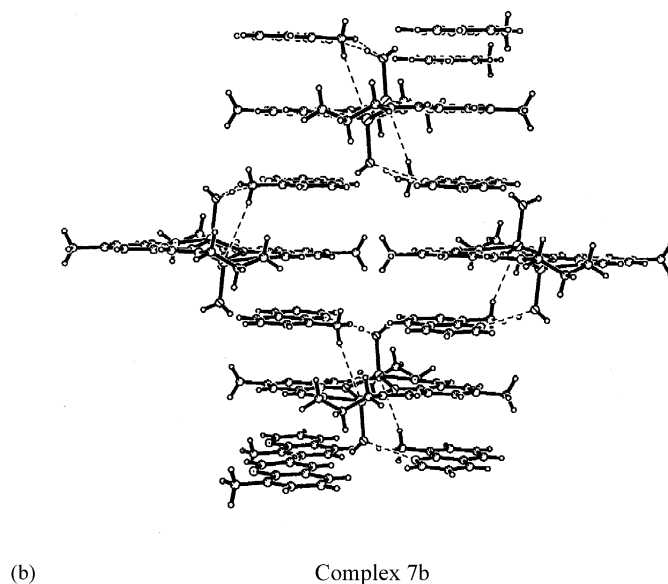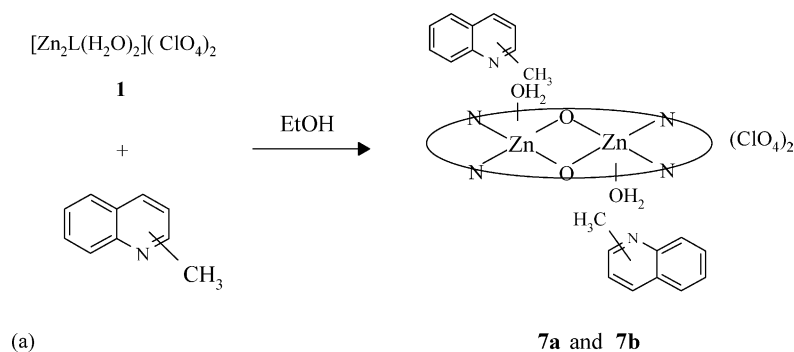
Fig. 7. (a) Self-assembly with alkyl substituted quinoline; (b) view of packing structure of **7b**.

H-bonding acceptor is also one oxygen atom of a perchlorate anion, but the former H-bonding donor comes from an ArCH=NR group of the macrocyclic framework and the latter from a pyridine unit. Similarly, in the case of 2,2′-bipyridine and pyridine, there seems to be no intermolecular interactions in **3a**, whereas in the crystal structure of **3b**, two adjacent chlorine atoms on benzene rings of two different macrocyclic frameworks and their α-positioned hydrogen atoms in the phenyl rings are involved in non-classical C−H···Cl intermolecular interactions in an end-to-end fashion. Thus a 1D chain structure is formed with the assistance of eight-membered ring structures containing two C−H···Cl H-bonds (Fig. 3(b)). Accordingly, the different packing in **3a** and **3b** arises from the different substituted groups on the phenyl rings.

Surprisingly, a hydrogen-bond cycle generated from the hydrogen atoms of two amino groups with two perchlorate anions has been observed in the assembling structure with 4-aminopyridine (Fig. 5(b)). Two hydrogen bonds of one anion group are a little different with H···O bond lengths of 2.346 and 2.213 Å, and N−H···O angles of 151.9 and

150.7°, respectively. In crystals, it is also observed that each perchlorate anion forms a non-classical and weak hydrogen bond (C−H···O) with a solvent molecule in addition to two strong N−H···O hydrogen bonds. The C−H···O H-bonding here has an O···H length of 2.575 Å comparable to those previously reported. Regarding the example of 4-PyCOO$^-$, two C−H···O types of hydrogen bonds are present in the crystal packing of **6a** (Fig. 6(b)). Both of the H-bonding acceptors are from the uncoordinated oxygen atom of 4-pyridine carboxylate anions, but the related H-bonding donors come from different sources: (1) from a methanol solvent molecule (H···O length = 2.473 Å and C−H···O angle = 107.33°); (2) from one carbon atom of the 1,3-propanediamino group of the macrocyclic framework (H···O length = 2.589 Å and C−H···O angle = 126.60°). These weak interactions have further stabilized the structure mentioned above.

Likewise, in the crystal packing of complexes **4a** and **4b**, C−H···O type H-bonding interactions are observed between the oxygen atom of the formate anion and the hydrogen atom from a phenyl ring of the macrocyclic unit (Fig. 4(b)). The geometric data for the H-bonding are 2.475 Å, 102.1° for **4a**
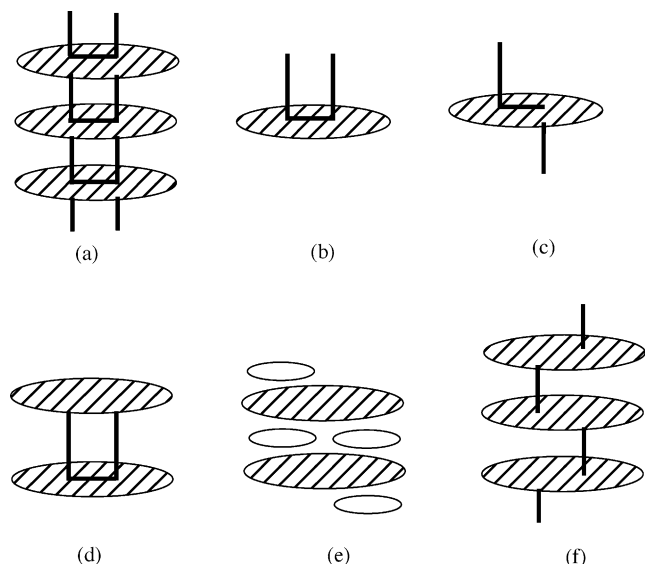
Fig. 8. Self-assembly with dinuclear zinc(II) complexes of Robson-type macrocycles: (a) molecular ladder composed of macrocyclic platforms and 4,4′-bipyridine bridges; (b) molecular ladder element with a macrocyclic base and 4-aminopyridine units; (c) supramolecular architecture in which two 4-aminopyridine units are placed in a *trans*-configuration of the macrocyclic platform; (d) wheel-like structural unit with μ_2-OH or 4-pyridinecarboxylate bridges; (e) donor–π–acceptor structural pattern without coordination bonding; (f) an infinite chain polymer with μ_2-formate bridges which are *trans* to the macrocyclic bases.

and 2.415 Å, 108.9° for **4b**, respectively. Both of the oxygen atoms of each formate anion take part in this kind of hydrogen bonding connecting two adjacent macrocyclic units. With the assistance of these weak interactions, ordered 2D networks are generated in the crystal structures of both **4a** and **4b**. Compared with our other complexes derived from **1b**, no C−H···Cl type H-bonding has been observed involving the chlorine atom on the top position of phenyl rings in **4b**.

7. Conclusions

The self-assembly of dinuclear zinc(II) macrocyclic complexes with various organic subunits (homobifunctional, heterobifunctional and monofunctional) has been extensively studied in our laboratory. So far, six kinds of dinuclear zinc(II) macrocyclic supramolecular arrays have been studied crystallographically (Fig. 8). A number of parameters associated with the organic ligands such as dimension, number of coordination sites and nature of coordination atom are revealed to play a key role in determining the architecture of the final product. For example, assembly with 4,4′-bipyridine resulted in a 1D molecular ladder whereas 2,2′-bipyridine yielded a discrete open-mouthed sandwich-like supramolecular complex lacking organic subunits. Similarly, a supramolecular species containing a molecular ladder motif was obtained for 4-aminopyridine in marked contrast to the wheel-like struc-

ture observed in the case of 4-pyridinecarboxylate. Additionally, a variety of hydrogen bonding patterns, in particular non-classical hydrogen bonding, were involved in the crystal stacking process. Such non-classical hydrogen e.g. C−H···Cl distinctly impact the architecture of the resulting compounds. A good instance for this point is the assembly of 4,4′-bipyridine in **2b**, wherein a 2D network is present compared with the 1D ladder with **2a** due to the participation of non-classical hydrogen bonding.

Acknowledgements

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