

## The Assembly of Supramolecular Boxes and Coordination Polymers Based on Bis-Zinc-Salphen Building Blocks

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**Abstract:** We report the assembly of supramolecular boxes and coordination polymers based on a rigid bis-zinc(II)-salphen complex and various ditopic nitrogen ligands. The use of the bis-zinc(II)-salphen building block in combination with small ditopic nitrogen ligands gave organic coordination polymers both in solution as well as in the solid state. Molecular modeling shows that supramolecular boxes with small

internal cavities can be formed. However, the inability to accommodate solvent molecules (such as toluene) in these cavities explains why coordination polymers are prevailing over well-

defined boxes, as it would lead to an energetically unfavorable vacuum. In contrast, for relatively longer ditopic nitrogen ligands, we observed the selective formation of supramolecular box assemblies in all cases studied. The approach can be easily extended to chiral analogues by using chiral ditopic nitrogen ligands.

**Keywords:** cage compounds • coordination polymers • self-assembly • supramolecular chemistry • template synthesis

### Introduction

Supramolecular chemistry has evolved into a mature field of science and a plethora of fascinating nano-sized structures can be prepared by self assembly. Self-assembled structures based on metal–ligand interactions have become increasingly important, as they are ideal tools for controlling geometry and dynamics. In addition, they provide new opportunities for introducing functionality.<sup>[1,2]</sup> As the field has matured, the focus has increasingly shifted from structural towards functional aspects. An important step towards the application of self-assembled structures, is the translation of the de-

fined solution structures to the solid state. An important research field that has attracted enormous interest in recent years is that of controlled porous materials and metallo-organic frameworks (MOFs).<sup>[3]</sup> The interest in these materials is fueled by the (potential) application in separation, recognition, absorption, sensing, and catalysis.<sup>[4–6]</sup> Coordination networks can be constructed from a variety of molecular building blocks applying different interactions that fix the building block in a specific well-defined orientation. As a consequence, this regularity facilitates design affording materials with specific properties. It is therefore not surprising that an increasing number of articles have appeared on the design of new porous architectures and some excellent reviews have reported on this subject.<sup>[7–11]</sup>

The design of new porous architectures requires the use of robust molecular building blocks, sometimes called tectons, which have the ability to form rigid networks through the presence of supramolecular interaction motifs (“synthons”).<sup>[12]</sup> Promising examples of these directional and strong recognition motifs constitute hydrogen bond interactions and metal–ligand interactions. Metalloporphyrins<sup>[13]</sup> have been shown to be versatile building blocks for the construction of these coordination networks.<sup>[14,15]</sup> Porphyrins are generally flat, rigid, and chemically and thermally stable building blocks. Moreover, metalloporphyrins have demonstrated catalytic activity in a variety of reactions, and thus the corresponding metalloporphyrin networks have the po-

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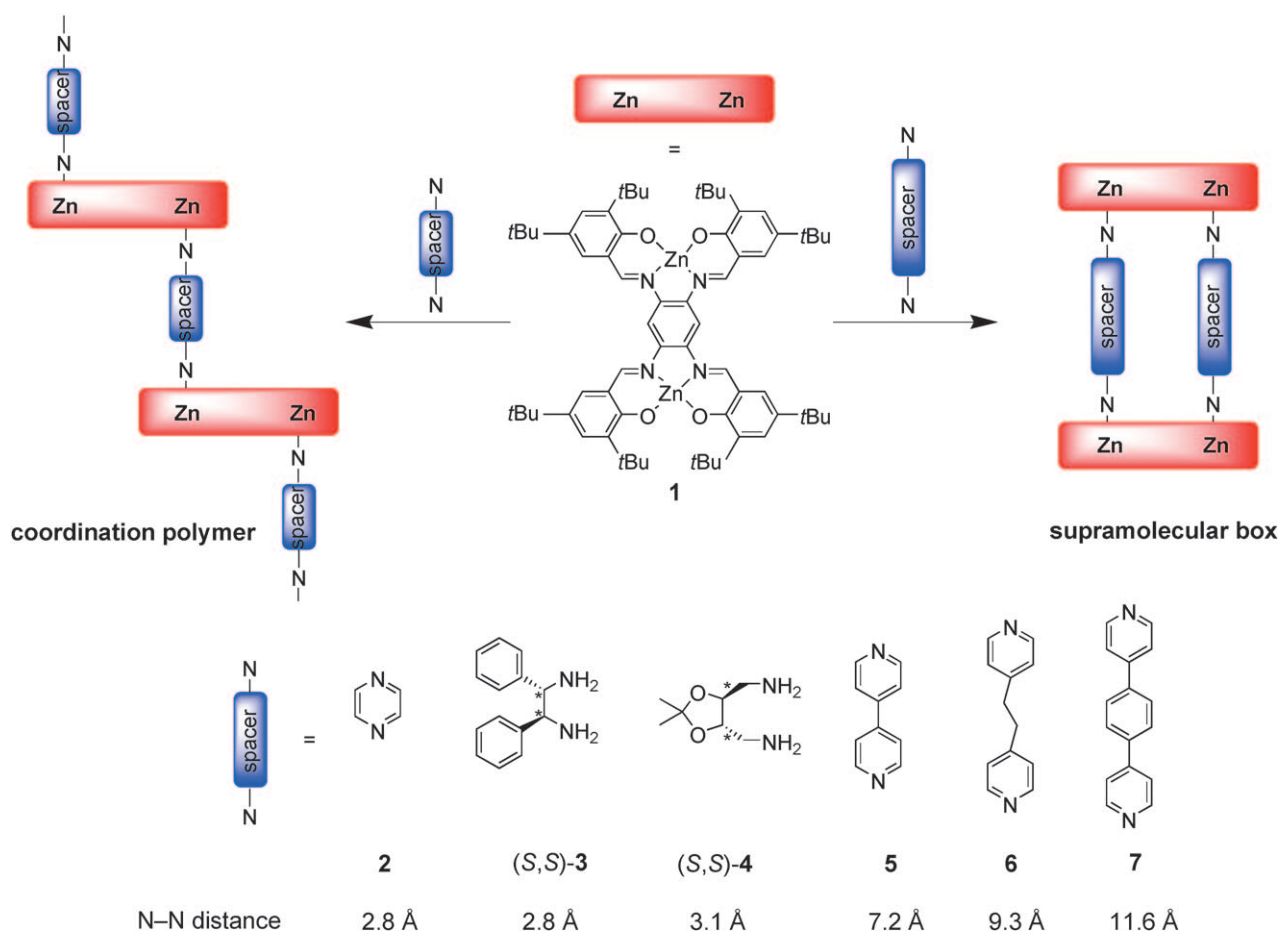
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tential to act as shape and size-selective heterogeneous catalysts.

The group of Goldberg<sup>[14,16]</sup> and others<sup>[15,17,18]</sup> reported some interesting porous porphyrin-based solids. Goldberg and co-workers mainly focused on *para*-carboxyphenyl substituted porphyrins affording a variety of framework solids resembling molecular sieves and zeolite materials. We recently showed that zinc(II) salen and salphen complexes are also very versatile building blocks in supramolecular chemistry.<sup>[19,20]</sup> These compounds are easy to prepare and are generally available in larger quantities than porphyrin building blocks. These building blocks also crystallize more easily. In a previous report,<sup>[20]</sup> we described the formation of supramolecular boxes based on bis-zinc(II)-salphen building block **1** and ditopic ligands such as bipyridine ligand **5**.<sup>[21]</sup> We found that the alignment of the boxes in the solid state results in the formation of porous materials. Varying the size of the cavities of these materials, by changing the length of the ditopic dinitrogen spacer, provides access to tunable frameworks that can be matched with the envisioned application. Here, we provide a detailed account of the relation between the structural properties of the supramolecular assembly and the molecular size of the ditopic ligands.

## Results and Discussion

Prior to the experimental studies, we first performed a theoretical analysis of the molecular boxes that can be assembled by applying building blocks of various sizes. A priori, one may expect that the formation of the relatively small box assemblies could be restricted as a result of steric crowding, and in these cases, suggest that alternative supramolecular structures are formed. However, based on molecular modeling calculations an assembly constructed from bis-zinc(II)-salphen complex **1** and pyrazine **2** (distance between the two nitrogen donor atoms = 2.8 Å) could still afford a supramolecular box assembly (Scheme 1), without significant steric repulsion between **1** and **2**. Indeed, the energies of the box assembly and that of open assembly (corrected for the number of atoms) are in the same range (Figure 1).<sup>[22]</sup> Pyrazine was therefore the building block that was chosen to study if small boxes, and perhaps porous materials with small pore size, could be prepared using the self-assembly approach. In addition, a similar sized molecular box was attempted, as well as a larger one, using chiral ditopic nitrogen ligands, which will give rise to chiral supramolecular box assemblies that are potentially useful in a



Scheme 1. Schematic view of the formation of organic coordination polymers or supramolecular box assemblies constructed from a bis-zinc(II)-salphen template in combination with ditopic nitrogen ligands with a variable distance between the two nitrogen donor atoms.

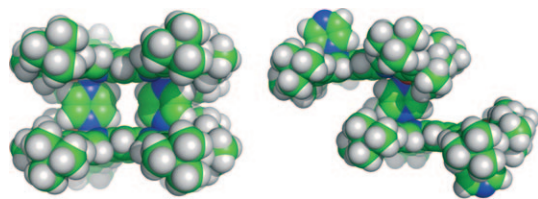


Figure 1. Modeled structures of the supramolecular box assembly  $(\mathbf{1})_2 \cdot (\mathbf{2})_2$  (left) and the repeating part of the coordination polymer  $(\mathbf{1})_2 \cdot (\mathbf{2})_3$  (right) (purple = Zn, blue = N, red = O, green = C and white = H).

number of applications (e.g., chiral separation, recognition, absorption, etc.).<sup>[23,24]</sup>

For the larger building blocks, one intuitively expects that coordination polymers will be formed rather than molecular boxes. To theoretically verify this, we analyzed our systems using the recently introduced effective concentration approach by Huskens et al.<sup>[25]</sup> As a starting point for this analysis we used the previously reported supramolecular box assembly based on a bis-zinc(II)-salphen building block **1** and 4,4'-bipyridine (bipy) ligand **5**.<sup>[20]</sup> The supramolecular box assembly consists of an 2:2 assembly with the simultaneous binding of two ditopic nitrogen ligands to two bis-zinc(II)-salphen building blocks. For the analysis of this binding event using the effective concentration ( $C_{\text{eff}}$ ), the binding process is separated in four steps, in each case forming a pyridine–zinc–coordinative bond. The first binding events are rather independent, as there is poor communication between the zinc centers of complex **1** on the one hand and the nitrogens of the bipy on the other. It is the last binding event that decides whether the molecular box or a coordination polymer is formed. The effective concentration, which can be estimated from the structure, is the concentration above which intermolecular binding is preferred over intramolecular binding leading to coordination polymers.<sup>[25]</sup> The effective concentration can be estimated from the volume in which both ends of the binding motif can move before they form the bond. For flexible systems this is easily done by using the maximum distance between the two parts of the binding motif as the radius to calculate the volume of the sphere. For our system it is more complicated as we have rigid building blocks. The solid ellipse in Figure 2 represents the rotational freedom of the bis-zinc(II)-salphen building block, and the corresponding volume is about  $436 \text{ \AA}^3$  ( $\pi \cdot (8.07)^2 \cdot 2.13 = 0.44 \times 10^{-24} \text{ dm}^3$ ). We doubled this volume as there is a second state (Figure 2) in which a similar rotation is possible with the second bipy coordinated to the other side. The effective concentration is then estimated by  $C_{\text{eff}} = 1 / ((6.02214 \times 10^{23}) \cdot (0.87 \times 10^{-24})) = 1.9 \text{ mol dm}^{-3}$ . The estimated effective concentration is much higher than the concentration of the ditopic nitrogen ligand in solution and therefore intramolecular binding is favored over the formation of oligomeric and polymeric structures in this case.<sup>[26]</sup> The effective concentration of assemblies  $(\mathbf{1})_2 \cdot (\mathbf{2})_2$  and  $(\mathbf{1})_2 \cdot (\mathbf{7})_2$  (both consisting of rigid ditopic nitrogen ligands) can be calculated in a similar manner providing similar values  $C_{\text{eff}} =$

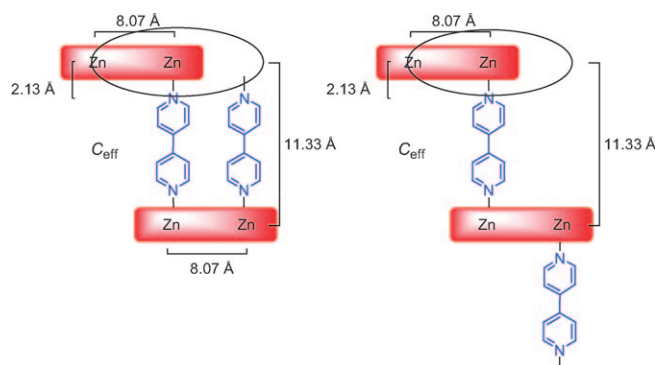


Figure 2. Schematic representation of the concept of effective concentration for assembly  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  in which the bis-zinc(II)-salphen can rotate, defining the volume, while the assembly can be in two states (left and right). For a detailed explanation, see text.

$1.9 \text{ mol dm}^{-3}$ .<sup>[25]</sup> This means that if rigid building blocks are used for the box assembly, the distance between the two nitrogen donor atoms has no influence on the effective concentration and as a consequence, we expect the formation of molecular boxes for a large series of rigid building blocks. On the other hand, the distance between the two zinc atoms will change the effective concentration, but in this contribution, we use the same bis-zinc(II)-salphen building block **1**.

With the effective concentration, one can also analyze whether the interactions involved in the assembly process show cooperativity or that the increased binding is a result of multivalency. In the current example, if the overall association constant ( $K$ ) deviates from  $K = k_1 \cdot k_2 \cdot k_3 \cdot k_4 \cdot C_{\text{eff}}$ , cooperativity can be assumed. We found that the overall constant is  $K \geq 10^{20} \text{ M}^{-3}$  and we know that the individual association constants are  $k_1 = k_2 = k_3 = k_4 \approx 10^5 \text{ M}^{-1}$ . The fact that we estimated the effective concentration of the system to be around 1 M, indicates that the interactions do not show cooperativity. An alternative way of looking at cooperativity effects uses the concept of effective molarity (EM). If a positive cooperative binding exists, then  $C_{\text{eff}}$  is larger than EM. The term effective molarity is defined as:  $\text{EM} = (K_n / (b \cdot K_i^n))^{1/(n-1)}$ , in which  $K_n$  is the association constant for an  $n$ -valent interaction,  $K_i$  is the intrinsic association constant and  $b$  is a scaling factor including statistical factors.<sup>[25,27,28]</sup> For our discrete 2:2 assemblies,  $K_i = 10^5 \text{ M}^{-1}$  and  $K_n \geq 10^{20} \text{ M}^{-3}$ , an effective molarity of  $(\geq 10^{20} / b \cdot (10^5)^4)^{1/3} = (\geq 1/b)^{1/3}$  could be calculated. This means that it is very likely to afford an effective molarity of at least  $1.9 \text{ mol dm}^{-3}$ , and as a consequence no cooperative binding exists in our case.

In previous studies we showed that the use of the bis-zinc(II)-salphen building block **1** in combination with various ditopic nitrogen ligands gave discrete 2:2 assemblies (Scheme 1). The structure of the supramolecular box assembly for assemblies  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  and  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$  was clearly confirmed by X-ray diffraction (Figure 3). The size of the molecular box is determined by the Zn–Zn distance within building block **1** (8.1 Å) and by the distance between the nitrogen donors of the ditopic ligand, which controls the dis-

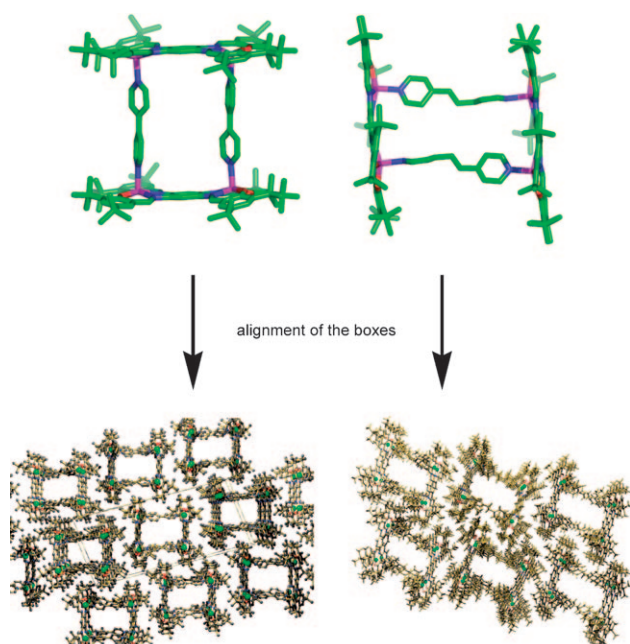


Figure 3. Top: Molecular structure of assemblies  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  (left) and  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$  (right) in the solid state. Co-crystallized solvent molecules and hydrogen atoms have been omitted for clarity (purple = Zn, blue = N, red = O, white = H, and green = C). Bottom: Packing of  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  (left) and  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$  (right) in the solid state, clearly showing the open channel structure (green = Zn, blue = N, red = O, and black = C; hydrogen atoms and disordered solvent molecules occupying the channels have been omitted for clarity, view along the YO).

tance between the two zinc(II)-salphen units (11.3 Å for  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  and 13.5 Å for  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$ ). This results in a box diameter of 13.9 Å (for  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$ )<sup>[29]</sup> and 15.7 Å (for  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$ )<sup>[30]</sup> respectively. The Zn–N<sub>pyr</sub> distance for  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  and  $(\mathbf{1})_2 \cdot (\mathbf{6})_2$  (~2.13 Å) is similar to that found for analogous pyridine salphen complexes.<sup>[31,32]</sup>

Interestingly, the packing of both molecular boxes leads to a porous material with channels in one direction along the crystallographic *b* axis (Figure 3 bottom). The use of other ditopic ligands and bis-zinc(II)-salphen building blocks should lead to porous materials with different controllable channel sizes. For example, molecular modeling predicts box sizes and thus channel dimensions for  $(\mathbf{1})_2 \cdot (\mathbf{7})_2$  of 15.5 × 8.1 Å (diameter ~17.4 Å). It is important to note that the box structures are formed by neutral building blocks, so that the channels are not blocked by counterions but contain disordered solvent molecules.

<sup>1</sup>H NMR spectroscopy as well as UV/Vis titration experiments of the bis-zinc(II)-salphen building block and 4,4'-bipyridine **5** supported the formation of a supramolecular box assembly in solution. The UV/Vis titration curve of the bis-zinc(II)-salphen building block and 4,4'-bipyridine **5** showed only one inflection point at a ratio of **1**:**5** = 1, suggesting that only a single species is present with a very high overall binding constant (see Supporting Information). The curve did not change beyond the inflection point, indicating that the molecular box assembly is the dominant species in solution,

also in the presence of excess bipy. Although we were unable to fit the titration curve,<sup>[33]</sup> we know that the overall association constant for the  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$  complex is at least  $10^{20} \text{ M}^{-3}$  because, at a concentration of  $1.1 \times 10^{-5} \text{ M}$ , more than 95 % is in the associated state. This is consistent with the simultaneous binding of two bipy ligands in the 2:2 assembly, and is clearly sufficiently strong to suppress the formation of other assemblies (i.e., oligomeric and polymeric structures).

The versatility of the approach to form box type structures in solution was supported by the use of two extended bipyridine ligands as ditopic components (**6** and **7**) thereby forming box structures with a larger diameter. Similar <sup>1</sup>H NMR behavior and UV/Vis titration curves (see Supporting Information) for these assemblies were observed as for  $(\mathbf{1})_2 \cdot (\mathbf{5})_2$ , and pointed at the formation of a discrete 2:2 assembly with a high association ( $> 10^{20} \text{ M}^{-3}$ ).<sup>[33]</sup>

We were interested if the assembly constructed from bis-zinc(II)-salphen complex **1** and pyrazine **2** would form a supramolecular box assembly with a small cavity or a coordination polymer. To investigate the assembly behavior of the bis-zinc(II)-salphen complex and pyrazine, we prepared crystals of the assembly that were suitable for X-ray diffraction experiments. The solid-state structure showed only the formation of a coordination polymer (Figure 4). The coordi-

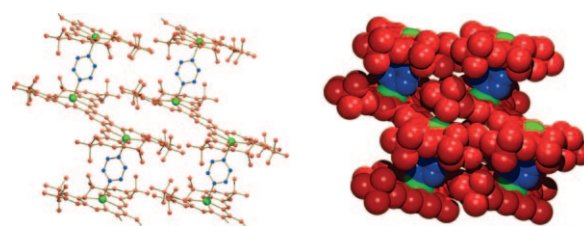


Figure 4. Packing of  $(\mathbf{1})_n \cdot (\mathbf{2})_n$  in the solid state, the polymeric structure is formed by proper alignment of the building blocks. Hydrogen atoms, the minor disordered component and co-crystallized solvent molecules have been omitted for clarity (green = Zn, red = bis-Zn-salphen complex, and blue = pyrazine).

nation of the ditopic pyrazine ligand per bis-zinc(II)-salphen building block occurs at opposite sides of the bis-salphen scaffold. The bis-zinc(II)-salphen molecules are aligned in a ladder-type manner (i.e., the bis-zinc(II)-salphen complexes align in a parallel fashion), in which no intercalation occurs between the different polymeric structures. The polymeric structure is stabilized through  $\pi$ - $\pi$  interactions between the different layers. The two bis-zinc(II)-salphen units are separated by 7.11 Å (Zn–Zn). The Zn–N<sub>pyr</sub> distance for the assembly  $(\mathbf{1})_n \cdot (\mathbf{2})_n$  is 2.167(2) Å, which is slightly longer as found for analogous pyridine salen complexes (2.10–2.14 Å).<sup>[31,32]</sup> These dimensions and distances correspond with the molecular modeling studies, only the connectivity between the building blocks differs.

To determine whether a coordination polymer is also present in solution, or if crystal packing effects account for



it, we performed UV/Vis titration experiments in solution (toluene,  $[1] = 1.7 \cdot 10^{-5} \text{ M}^{-1}$ ). The UV/Vis titration curve for bis-zinc(II)-salphen and pyrazine showed one inflection point at a ratio of  $1:2=1$  (see the Supporting Information). However, in contrast to the curve obtained for  $(1)_2 \cdot (5)_2$ , the curve increased gradually beyond the inflection point, which suggests that multiple species are present in solution.<sup>[33]</sup> The change in absorption after the inflection point indicates the presence or the formation of different species among which are open structures, oligomeric, and polymeric structures.

Although molecular modeling studies showed that the formation of a coordination polymer and a supramolecular box assembly are both possible (vide supra), that is, not prevented by steric hindrance between the building blocks involved, we only observed the formation of a polymeric structure in the solid state. We also did not find indications of exclusive box formation in solution. The most likely explanation is that the solvent molecules used (toluene) are too large to fit in the cavity. Molecular modeling suggests that this indeed is the case for toluene, and the boxes might be formed if smaller solvents are used. This relates to the formation of molecular capsules that generally also only form in the presence of a suitable guest.<sup>[34]</sup> Molecular modeling indeed shows that nitromethane as solvent fits well in the cavity of  $(1)_2 \cdot (2)_2$  (see the Supporting Information). Although this structure shows that these small molecules at least fit inside, it does not provide information on how well the cavity containing structure is solubilized compared to the open structure.

To arrive at chiral supramolecular assemblies, we used the bis-zinc(II)-salphen building block in combination with chiral ditopic nitrogen ligands. In analogy to  $(1)_n \cdot (\text{pyrazine})_n$ , the solid state structure for  $(1)_n \cdot ((S,S)\text{-}1,2\text{-diphenylethylamine})_n$  showed a polymeric structure (Figure 5). Obviously,

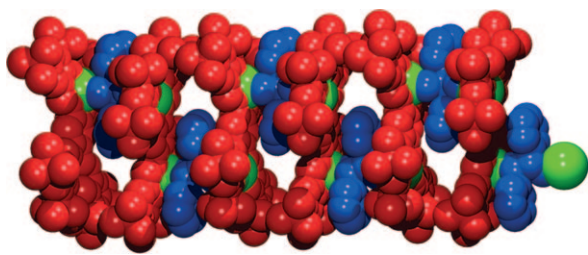


Figure 5. Top: Packing of  $(1)_n \cdot ((S,S)\text{-}3)_n$  in the solid state, the polymeric structure is formed by proper alignment of the building blocks. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity (green = Zn, blue = N, red = O, and black = C). Bottom: 3-D view of the packing of  $(1)_n \cdot ((S,S)\text{-}3)_n$  (green = Zn, red = bis-Zn-salphen building block, blue =  $(S,S)\text{-}3$ ).

now a chiral coordination polymer is obtained in which the absolute configuration of the diamine ligand  $(S,S)$  is confirmed. In spite of the steric bulk imposed by the two phenyl groups of the  $(S,S)\text{-}1,2\text{-diphenylethylamine}$  ligand, the  $\text{Zn}-\text{N}_{\text{amine}}$  distance was only  $2.13 \text{ \AA}$ ,<sup>[35]</sup> which is slightly shorter compared to the  $\text{Zn}-\text{N}_{\text{pyr}}$  distances for  $(1)_n \cdot (2)_n$

( $2.17 \text{ \AA}$ ). The  $\text{Zn}-\text{Zn}$  distance between the two bis-zinc(II)-salphen building blocks connected by the ditopic nitrogen ligand is  $7.36 \text{ \AA}$ .<sup>[36]</sup>

A more important difference between the two assemblies is the arrangement of the bis-zinc(II)-salphen building blocks. Whereas in  $(1)_n \cdot (2)_n$ , the bis-zinc(II)-salphen molecules are aligned in a ladder-type manner (i.e., the bis-zinc(II)-salphen complexes align in a parallel fashion, see Figure 4), in  $(1)_n \cdot ((S,S)\text{-}3)_n$  the structure is slightly tilted and the bis-zinc(II)-salphen building blocks are aligned in a zigzag fashion (see Figure 5). This is ascribed to the size of the ditopic nitrogen ligand. Apparently there is insufficient space between the two bis-zinc(II)-salphen units to host two molecules of **3**.

The formation of a polymeric structure for assembly  $(1)_n \cdot ((S,S)\text{-}3)_n$  was also observed in solution by means of UV/Vis titration experiments (toluene), which showed a different type of curve as compared to the supramolecular box assemblies. The UV/Vis titration curve for bis-zinc(II)-salphen **1** and  $(S,S)\text{-}1,2\text{-diphenylethylamine}$  showed only one inflection point at a ratio of  $1:(S,S)\text{-}3=1$  (see supporting information). It should be noted that the curve still increased gradually beyond the inflection point, which suggests the presence of multiple species in solution.<sup>[33]</sup>

To invoke enough space for solvent molecules to enter the space between the two bis-zinc(II)-salphen building blocks, we also used a chiral ditopic nitrogen ligand in which the distance between the nitrogen donors is longer. Indeed, the UV/Vis titration curve of bis-zinc(II)-salphen building block **1** and  $(4S,5S)\text{-}4,5\text{-di(aminomethyl)-}2,2\text{-dimethyldioxolane}$  **4** showed only one inflection point at a ratio of  $1:4=1$  (see the Supporting Information). Consistent with a 2:2 assembly in solution, the titration curve showed virtually no increase beyond the inflection point indicating that a single species is present in solution, which is stable in the presence of a small excess of **4**. Precise fitting of the titration curve was too complicated as too many binding processes are involved, but from the curve we estimate an overall association constant for the  $(1)_2 \cdot ((4S,5S)\text{-}4)_2$  complex which is at least  $10^{20} \text{ M}^{-3}$ .<sup>[33]</sup> This is consistent with the simultaneous binding of two ditopic nitrogen ligands **4** in the 2:2 assembly, and is in line with the results found previously for  $(1)_2 \cdot (5)_2$ ,  $(1)_2 \cdot (6)_2$ , and  $(1)_2 \cdot (7)_2$ . Unfortunately, we were unable to grow crystals of sufficient quality from the assembly  $(1)_2 \cdot ((4S,5S)\text{-}4)_2$ , but molecular modeling predicts box sizes and thus channel dimensions for  $(1)_2 \cdot ((4S,5S)\text{-}4)_2$  of  $9.7 \times 8.1 \text{ \AA}$  (diameter  $12.5 \text{ \AA}$ , Figure 6). The important thing to note here is that chiral supramolecular box assemblies based on **1** are thus feasible as long as the chiral spacer can accommodate the formation of a 2:2 assembly. This opens up ways to create new chiral porous materials for various applications.<sup>[23,24]</sup> An important prerequisite is that both nitrogen donor atoms have similar association constants with the Lewis acidic  $\text{Zn}^{\text{II}}$  atom. For instance, the use of the dipeptide  $\text{H}_2\text{N-Gly-His-OMe}$  possessing two nitrogen donor atoms (i.e., an  $\text{NH}_2$ -group and an imidazole-unit) with different association constants in combination with the bis-

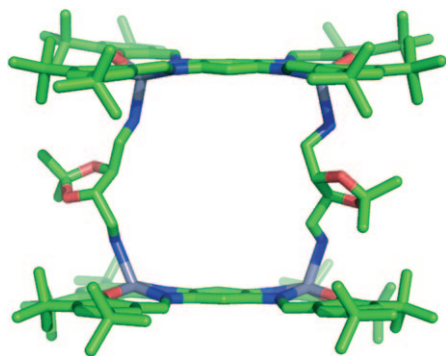


Figure 6. Modeled structure of the supramolecular box assembly  $(1)_2 \cdot ((4S,5S)-4)_2$ . Hydrogen atoms have been omitted for clarity (purple = Zn, blue = N, red = O and green = C).

zinc(II)-salphen building block gave various species in solution in the presence of excess dipeptide.

## Conclusions

We have demonstrated that the bis-zinc(II)-salphen complex is an excellent building block for the formation of well-defined structures in solution as well as in the solid state. In combination with a variety of ditopic nitrogen ligands, the complex was shown to form either coordination polymers or (chiral) supramolecular box assemblies. As expected, ditopic nitrogen ligands, with a longer distance between the two nitrogen donors, in combination with the bis-zinc(II)-salphen building block gave 2:2 supramolecular box assemblies both in solution and in the solid state. Interestingly, the molecular boxes line-up in the solid state, providing solid-state materials with channels in one direction. The formation of molecular boxes is not limited to rigid ligands as flexible ligands, like 1,2-bis(4-pyridyl)ethane, could result in molecular boxes and porous solid materials, with slightly larger channel sizes. In the search for materials with smaller sizes we explored various ditopic nitrogen ligands with a relative short distance between the two nitrogen donors. According to molecular modeling these could also give molecular boxes, and potentially porous solid materials, when assembled to the bis-zinc(II)-salphen. Unexpectedly, these complexes afforded organic coordination polymers in the solid state, and also in solution as there was no evidence for unique molecular box formation. Likely, solvation of the inner structure of the molecular box plays a crucial role. Solvent molecules, such as toluene, are unable to occupy the cavities provided upon formation of small supramolecular box assemblies, and as a result, the formation of coordination polymers is favored. Currently, the lower limit in size are boxes and porous materials thereof, with dimensions of  $8 \times 13$  Å. Interestingly, the strategy is easily extended to chiral supramolecular boxes such as assembly  $(1)_2 \cdot ((4S,5S)-4,5\text{-di(aminomethyl)-2,2-dimethyldioxolane})_2$ . These (chiral) supramolecular box as-

semblies are potentially useful for chiral separations, which we are currently exploring.<sup>[37]</sup>

## Experimental Section

### General

Molecular modeling was performed using semi-empirical (PM3-tm) calculations using the Spartan software or the Titan software. All reagents were purchased from commercial suppliers and used without further purification. The bis-Zn<sup>II</sup>-salphen complex **1** was synthesized according to a published procedure.<sup>[20]</sup> The crystal structures  $(1)_2 \cdot (5)_2$  and  $(1)_2 \cdot (6)_2$  were published previously.<sup>[20]</sup> Both  $(1)_n \cdot (2)_n$  and  $(1)_n \cdot (3)_n$  were crystallized from a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ .

### Crystal Structure Determination

X-ray intensities were collected on a Nonius KappaCCD diffractometer with rotating anode and  $\text{MoK}\alpha$  radiation (graphite monochromator,  $\lambda = 0.71073$  Å) at a temperature of 150(2) K. The structures were solved by Patterson methods (DIRDIF99<sup>[38]</sup> for  $(1)_n \cdot (2)_n$  and  $(1)_n \cdot ((S,S)-3)_n$  and refined with SHELXL-97<sup>[39]</sup> against  $F^2$  for all reflections. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.<sup>[40]</sup> Where present, disordered solvent molecules were taken into account by back-Fourier transformation with PLATON-SQUEEZE.<sup>[41]</sup>

X-ray crystal structure determination of  $(1)_n \cdot (2)_n$ :  $\text{C}_{66}\text{H}_{86}\text{N}_4\text{O}_4\text{Zn}_2 + \text{C}_4\text{H}_4\text{N}_2 + \text{disordered solvent}$ ,  $M_r = 1210.26$  [\*],  $0.09 \times 0.20 \times 0.25$  mm<sup>3</sup>; triclinic,  $P\bar{1}$  (no. 2);  $a = 11.314(2)$ ,  $b = 11.393(3)$ ,  $c = 14.964(3)$  Å,  $\alpha = 103.942(18)^\circ$ ,  $\beta = 94.954(15)^\circ$ ,  $\gamma = 106.655(13)^\circ$ ,  $V = 1768.3(7)$  Å<sup>3</sup>;  $Z = 1$ ,  $\rho = 1.137$  g cm<sup>-3</sup> [\*],  $\mu = 0.725$  mm<sup>-1</sup> [\*]; 40808 reflections were measured up to a resolution of  $(\sin\theta/\lambda)_{\text{max}} = 0.59$  Å<sup>-1</sup>. An absorption correction based on multiple measured reflections was applied (correction range 0.60–0.94); 6245 reflections were unique ( $R_{\text{int}} = 0.067$ ). The unit cell contains two voids with a solvent accessible volume of about 127 Å<sup>3</sup>. A difference Fourier map indicated the presence of disordered  $\text{CH}_2\text{Cl}_2$ . Their contribution to the structure factors was secured by back-Fourier transformation with the SQUEEZE procedure in the program PLATON. A total of 35 electrons were recovered with this procedure per void, consistent with approximately one  $\text{CH}_2\text{Cl}_2$  molecule. 413 Refined parameters, 42 restraints;  $R$  (5010 reflections  $F > 4\sigma(F)$ ):  $R1 = 0.0467$ ,  $wR2 = 0.1075$ ;  $R$  (all data):  $R1 = 0.0561$ ,  $wR2 = 0.1135$ ;  $\text{GOF} = 1.049$ ; residual electron density between  $-0.33$  and  $0.46$  e Å<sup>-3</sup>. Note that the asterisk behind some of the numerical crystallographic data denotes the values without the contribution of the disordered solvent molecules. CCDC 693460 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

X-ray crystal structure determination of  $(1)_n \cdot (3)_n$ :  $\text{C}_{132}\text{H}_{172}\text{N}_8\text{O}_8\text{Zn}_4 + \text{C}_{28}\text{H}_{32}\text{N}_4 + \text{disordered solvent}$ ,  $M_r = 2684.93$  [\*], orange-red block  $0.05 \times 0.08 \times 0.22$  mm<sup>3</sup>; monoclinic,  $P2_1$  (no. 4);  $a = 13.8348(5)$ ,  $b = 39.310(2)$ ,  $c = 15.3517(8)$  Å,  $\beta = 93.328(2)^\circ$ ,  $V = 8334.9(7)$  Å<sup>3</sup>;  $Z = 2$ ,  $\rho = 1.070$  g cm<sup>-3</sup> [\*],  $\mu = 0.622$  mm<sup>-1</sup> [\*]; 21799 reflections were measured up to a resolution of  $(\sin\theta/\lambda)_{\text{max}} = 0.54$  Å<sup>-1</sup>. An absorption correction based on multiple measured reflections was applied (correction range 0.81–0.97); 21799 reflections were unique. The unit cell contains four voids with a solvent accessible volume of about 280 Å<sup>3</sup> and four voids with a volume in the range of 112 to 144 Å<sup>3</sup>. The difference map did not give a clear indication of the nature of their disordered content that was taken into account with the PLATON/SQUEEZE procedure. 65 and 32 electrons were recovered from the two types of voids, consistent with about 12 disordered  $\text{CH}_2\text{Cl}_2$  molecules in the unit cell. 806 Refined parameters, 1169 restraints;  $R$  (14936 reflections  $F > 4\sigma(F)$ ):  $R1 = 0.0609$ ,  $wR2 = 0.1474$ ;  $R$  (all data):  $R1 = 0.0876$ ,  $wR2 = 0.1603$ ;  $\text{GOF} = 1.066$ ; residual electron density between  $-0.40$  and  $0.69$  e Å<sup>-3</sup>. Note that the asterisk behind some of the numerical, crystallographic data denotes the values without the contribution of the disordered solvent molecules.

CCDC 693461 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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