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# Interpenetrated constitutional networks of aromatic metallosupramolecular duplexes

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We report hierarchical supramolecular organisation promoted by the formation of metallosupramolecular duplex architectures. Three-dimensional supramolecular structure propagation is favoured by long-range aromatic–aromatic interactions towards robust double-helical configuration in $\mathbf{1}_2\mathrm{Zn}^{2+}$, tubular squared architecture in $\mathbf{2}_2\mathrm{Zn}^{2+}$ and self-organised triangles in $\mathbf{4}_2\mathrm{Zn}^{2+}$. The advantageous structural features of such external aromatic interactions are not preserved while introducing new variables such as methylene spacer between imine moiety and the aromatic rings, inducing an orthogonal spatial orientation of the peripheral aromatic arms in $\mathbf{3}_2\mathrm{Zn}^{2+}$. Indeed, the introduction of supplementary aromatic functionality in $\mathbf{4}_2\mathrm{Zn}^{2+}$ results in the combination of both internal and external forces and has led to metallosupramolecular triangle architectures that are stabilised by three-dimensional 'diphenylmethane embrace motifs'. The homochiral triangles connected via tetrahedral nodes and face-to-face triangle interactions are organised in the crystal that each duplex constituent has an alternative opposite chirality.

**Keywords:** metallosupramolecular complexes; imine; self-assembly; aromatic interactions

## Introduction

Molecular self-organisation is the basis for the construction of new useful synthetic materials in a bottom-up strategy. The way from molecular- to nano(micro)-scale systems depends both on the nature of its constituents and on the interactions between them (*1–4*). The self-organisation exploits non-covalent interactions in a multitude of ways and implements sets of molecules containing specific information stored in the arrangement of specific binding sites. The selection of one or more supramolecular architectures occurs as a function of either internal (such as the nature and the geometry of the binding subunits, the composition, etc.) or external (such as the nature of the medium, the presence of specific molecules or anions, etc.) factors. Metal-directed self-assembly (*3–5*) or combined hydrogen-bonding–metal coordination (*6*) and $\pi-\pi$ stacking-metal coordination (*7*) supramolecular interactions has been extensively used as a powerful tool for the spontaneous generation of such nanostructures.

We have recently reported the double-helical complex $\mathbf{1}_2\mathrm{Zn}^{2+}$ (Figure 1(a)) which after being left to stand for some hours produced homochiral crystals containing only one of $\Delta$ and $\Lambda$ mirror enantiomers (*8*). In the crystal of $\mathbf{1}_2\mathrm{Zn}^{2+}$ each duplex of one helical sense is $\pi-\pi$ stacked with two duplexes of the same helical sense (Figure 1(b)). This pattern generates double-helical stacks of $\mathbf{1}_2\mathrm{Zn}^{2+}$ units. In the crystal, the adjacent columns of one helical sense run in parallel directions and interweave the peripheral phenyl and pyridine rings that are in van der Waals contact in a one-over/one-under fashion (Figure 1(c)). This generates a gearwheels-type mechanism with a very uncommon topology such that each double helix is in van der Waals contact with four neighbouring ones of the same helical sense.

A set of interconverting $\Delta$ and $\Lambda$ mirror enantiomers of $\mathbf{1}_2\mathrm{Zn}^{2+}$ units represents a constitutional dynamic library (*8c,d*) in solution. After some hours, single crystals started to form in the acetonitrile/*i*-propylether system and resolved homochiral metallosupramolecular domains of unique helicity had been amplified through a phase-change-driven selection process (*8d*). Constitutional affinity drives the selection of interdigitated homochiral double-helical architectures under internal pressure of the three-dimensional long-range multi-screw-type interactions (Figure 1(d)). Weak aromatic interactions stabilise such supramolecular assemblies by $\pi$-stacking and van der Waals aromatic interactions and constitute the driving force of the homochiral crystal phase cohesion.

To obtain systematic insights into the creation of these architectures interacting via peripheral aromatic groups, which are responsible for the constitutional communication between homochiral double-helical columns within the three-dimensional crystalline space, we investigated new similar systems by combining metal–ion coordination with weak aromatic–aromatic

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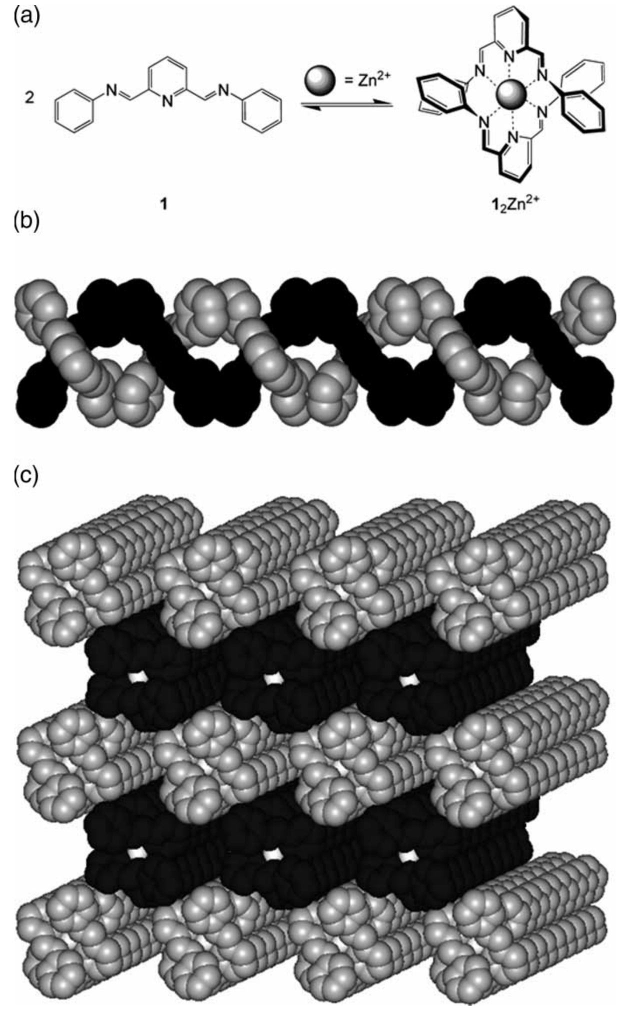


Figure 1. From achiral ligands to metallosupramolecular homochiral double-helical strands. (a) Synthesis of $\mathbf{1}_2Zn^{2+}$ duplex complexes, (b) homochiral double-helical stacks of $\mathbf{1}_2Zn^{2+}$ units and (c) crystal packing of double-helical columns: generation a *gearwheels-type* mechanism such that each double helix is in van der Waals contact with four neighbouring ones of the same helical sense.

interactions. As a step towards this goal, it is of interest to investigate whether changes in the expression of the crystal packing can be modulated by considering *outer structural factors*, by introducing different aromatic substituents on the peripheral surface (*9*). One possible presumption is to consider that the additional supramolecular aromatic interactions like that in biphenyl-type compound **2** or different spatial orientation of phenyl moiety like that in the benzyl-type compound **3** or supplementary hydrophobic interactions in the bisphenylmethane-type compound **4** might direct the constitutional organisation of the crystalline frameworks by controlling the supramolecular connectivity between the ligands of the metallosupramolecular duplexes $\mathbf{2}_2Zn^{2+}$, $\mathbf{3}_2Zn^{2+}$ and $\mathbf{4}_2Zn^{2+}$ (Scheme 1).

## Experimental section

### *Materials and methods*

2,6-Pyridinedicarboxaldehyde was prepared by oxidation of 2,6-pyridinemethanol with activated $MnO_2$ according to the procedure described in the literature (*11a*). 4-Aminobiphenyl, benzylamine benzhydrylamine were purchased from Aldrich (Milwaukee, WI, USA) and used as received. All other reagents were obtained from commercial suppliers and used without further purification. All organic solutions were routinely dried by using sodium sulphate ($Na_2SO_4$). $^1H$ and $^{13}C$ NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$ with the use of the residual solvent peak as reference. The assignments were made on the base of the COSY and NOESY spectra. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform II). Samples were continuously introduced into the mass spectrometer through a Waters 616HPLC pump. The temperature (60°C) and the extraction cone voltage ($V_c = 5-10$ V) were usually set to avoid fragmentations.

### *Synthesis of ligands 1–4*

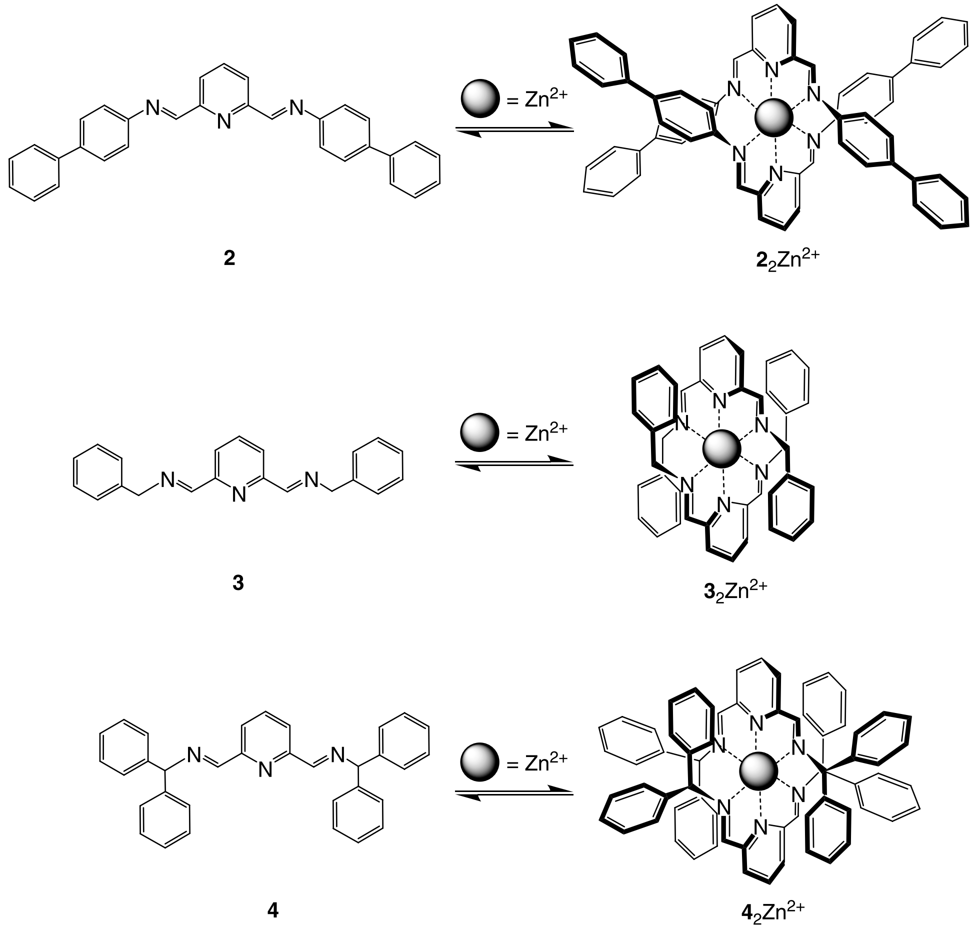
Ligands **1** (*11*) and **3** (*12*) were synthesised as previously described.

Ligand **2** has been synthesised in EtOH by condensation of 2,6-pyridinedicarboxaldehyde (0.1 g, 0.74 mmol) with 4-aminobiphenyl (0.25 g, 1.48 mmol), under reflux for 12 h with constant stirring. After solvent evaporation, the resulting crude material was recrystallised from acetonitrile to give **2** as a light-yellow solid (0.275 g, 85%). F.M. $C_{31}H_{23}N_3$, MW = 437.55 g/mol. $^1H$ NMR (300 Hz, $CDCl_3$, ppm): $\delta = 8.769$ (s, 2H, CH=N), 8.347–8.321 (d, 2H, $H^b$, $J = 7.8$ Hz), 8.005–7.952 (t, 1H, $H^a$, $J = 7.8$ Hz), 7.696–7.632 (m, 8H, $H^{c+d}$), 7.488–7.338 (m, 10H, $H^{ar}$). MS (ESI): *m/z* (100%): 438.25 ($\mathbf{2}$-$H^+$).

Ligand **4** has been synthesised in EtOH by condensation of 2,6-pyridinedicarboxaldehyde (0.1 g, 0.74 mmol) with benzhydrylamine (0.27 g, 1.48 mmol), under reflux for 12 h with constant stirring. After solvent evaporation, the resulting crude material was recrystallised from acetonitrile to give **4** as a white solid (0.310 g, 90%). F.M. $C_{33}H_{27}N_3$, MW = 465.59 g/mol. $^1H$ NMR (300 Hz, $CDCl_3$, ppm): $\delta = 8.530$ (s, 2H, CH=N), 8.273–8.248 (d, 2H, $H^b$, $J = 7.5$ Hz), 7.848–7.796 (t, 1H, $H^a$, $J = 7.8$ Hz), 7.404–7.217 (m, 20H, $H^{ar}$), 5.700 (s, 2H, CH). MS (ESI): *m/z* (100%): 466.29 ($\mathbf{4}$-$H^+$).

### *Synthesis and single crystal structures of $1_2Zn^{2+}$–$4_2Zn^{2+}$ complexes*

The reactions were performed typically on a 10 mg scale of ligand. The ligands **1–4** and $Zn(CF_3SO_3)_2$ were



Scheme 1. Synthesis of $\mathbf{2}_2\mathrm{Zn}^{2+}$, $\mathbf{3}_2\mathrm{Zn}^{2+}$ and $\mathbf{4}_2\mathrm{Zn}^{2+}$ duplex complexes.

dissolved in $CD_3CN$ (1 ml), and stirred overnight at 60°C. Layering such solutions of duplex complexes $\mathbf{1}_2\mathrm{Zn}^{2+}$–$\mathbf{4}_2\mathrm{Zn}^{2+}$ in acetonitrile with the *i*-propylether at room temperature, resulted in a unique set of single crystals suitable for X-ray single-crystal experiments.

*Compound* $\mathbf{1}_2Zn^{2+}$

$^1$H NMR ($CD_3CN$, ppm): $\delta = 8.82$ (s, 4H, CH═N), 8.60–8.55 (t, 2H, $H^a$, $J = 7.8$ Hz), 8.27–8.24 (d, 4H, $H^b$, $J = 7.8$ Hz), 7.38–7.25 (m, 12H, $H^{ar}$, $J = 8.7$ Hz), 6.91–6.88 (d, 8H, $H^{ar}$, $J = 3.35$ Hz). ES-MS: *m*/*z* (%): 317.7 (100).

*Compound* $\mathbf{2}_2Zn^{2+}$

$^1$H NMR ($CD_3CN$, ppm): $\delta = 8.901$ (s, 4H, CH═N), 8.626–8.574 (t, 2H, $H^a$, $J = 7.8$ Hz), 8.297–8.271 (d, 4H, $H^b$, $J = 7.8$ Hz), 7.631–7.414 (m, 32H, $H^d + H^{ar}$, $J^{d-c} = 8.4$ Hz), 6.923–6.895 (d, 8H, $H^c$, $J^{c-d} = 8.4$ Hz). ES-MS: *m*/*z* (%): 469.46 (100).

*Compound* $\mathbf{3}_2Zn^{2+}$

$^1$H NMR ($CDCl_3$, ppm): $\delta = 8.62$–8.58 (t, 2H, $H^a$, $J = 7.8$ Hz), 8.05 (s, 2H, CH═N), 7.85–7.80 (d, 2H, $H^b$), 7.20–7.10 (t, 2H, $H^{ar}$), 7.05–6.95 (t, 4H, $H^{ar}$), 6.65–6.55 (d, 4H, $H^{ar}$), 4.60 (s, 8H, $CH_2$). ES-MS: *m*/*z* (%): 373.7 (100).

*Compound* $\mathbf{4}_2Zn^{2+}$

$^1$H NMR ($CD_3CN$, ppm): $\delta = 8.244$–8.192 (t, 2H, $J = 7.8$ Hz), 7.935–7.927 (atropisomerism at room temperature, see text) (s, 4H, CH═N), 7.692–7.666 (d, 4H, $J = 7.8$ Hz), 7.210–7.112 (m, 40H, $H^{ar}$), 5.548–5.540 (atropisomerism at room temperature, see text) (s, 4H, CH). ES-MS: *m*/*z* (%):497.54 (100).

### *X-ray single crystal diffraction data for $\mathbf{1}_2Zn^{2+}$–$\mathbf{5}_2Zn^{2+}$, $\mathbf{1}_2Fe^{2+}$ and $\mathbf{1}_2Co^{2+}$ complexes*

The diffraction intensities were collected at the joint X-ray Scattering Service of the Institut Charles Gerhardt and the

Institut Européen des Membranes of the University of Montpellier II, France, at 175 K using an Oxford Diffraction Xcalibur-I and a Gemini-S diffractometer. The crystal-to-detector distance was 50 mm for all five measurements. The structures were solved by direct methods using SIR2002 (*13a*) or by *ab initio* (charge-flipping) methods using SUPERFLIP (*13b*) and refined by least-squares methods on $F$ using CRYSTALS (*13c*), against $|F|$ on data having $I > 2\sigma(I)$; $R$-factors are based on these data. Hydrogen atoms were partly located from difference Fourier synthesis, partly placed based on geometrical arguments, and in general not refined. Non-hydrogen atoms were in general refined anisotropically, except where the data to parameter ration did not allow doing this. Full details can be found in the cif-files and in Supplementary Material.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-695886-695888. Copies of the data can be obtained free of charge on application to CCDC, Cambridge, UK. E-mail: deposit@ccdc.cam.ac.uk.

## Results and discussion

The crystal structures of the complexes $\mathbf{2}_2\mathrm{Zn}^{2+}$, $\mathbf{3}_2\mathrm{Zn}^{2+}$ and $\mathbf{4}_2\mathrm{Zn}^{2+}$ were determined from crystals obtained from the acetonitrile/*i*-propylether solutions at room temperature. The molecular and crystal packing structures are presented in Figures 2 and 3. In all duplex structures of $\mathbf{2}_2\mathrm{Zn}^{2+}$, $\mathbf{3}_2\mathrm{Zn}^{2+}$ and $\mathbf{4}_2\mathrm{Zn}^{2+}$, the $\mathrm{Zn}^{2+}$ ions are fully coordinated by two ligands arranged into two orthogonal planes and present an octahedral coordination geometry (Figure 2). The average $\mathrm{Zn}^{2+}-\mathrm{N}_{\mathrm{Pyridine}}$, $\mathrm{Zn}^{2+}-\mathrm{N}_{\mathrm{imine}}$ and $\mathrm{Zn}^{2+}-\mathrm{N}_{\mathrm{imine}}$ distances are 2.05 or 2.24 Å, respectively.

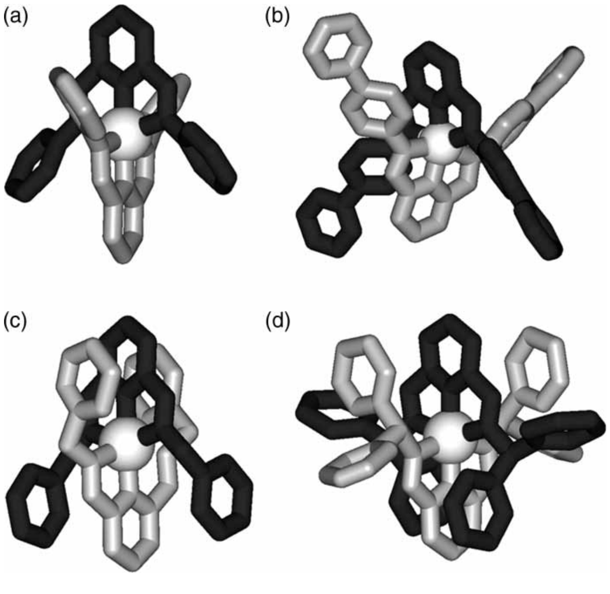


Figure 2. Crystal structure in stick representation of the duplex complexes (a) $\mathbf{1}_2\mathrm{Zn}^{2+}$, (b) $\mathbf{2}_2\mathrm{Zn}^{2+}$, (c) $\mathbf{3}_2\mathrm{Zn}^{2+}$ and (d) $\mathbf{4}_2\mathrm{Zn}^{2+}$; the $\mathrm{Zn}^{2+}$ ions are shown as white spheres.

The unit cell of $\mathbf{2}_2\mathrm{Zn}^{2+}$ was found to contain six homoduplex complexes together with 12 triflate counterions. Overall, the crystal structure is racemic and the duplexes are organised in parallel layers of $\Delta$ and $\Lambda$ mirror enantiomers, which are alternatively stratified. Within a layer, they are associated by two different sets of $\pi-\pi$ stacking interactions (Figure 3(a)).

These aromatic stacking interactions are constitutionally different and allow in one direction the internal overlaps between the biphenyl–pyridine triads with the average centroid–centroid distances of 3.71 and 3.98 Å corresponding to van der Waals contact. The terminal phenyl moiety of the biphenyl triad in further $\pi-\pi$ stacked with a similar one of the adjacent layer (the average centroid–centroid distance of 3.94 Å). In the other direction, each layer is alternatively stratified above each other by stacking only the terminal biphenyl moieties, such that each layer is in van der Waals contact (the average centroid–centroid distance of 4.10 Å). The square packing arrangement of duplex subunits results in the formation of a tubular structure with a hydrophobic hole of approximately 3 Å. The triflate anions are arranged into approximate linear array tightly fitting into the central cavity of the resulted tubular channels (Figure 3(b)).

As expected, the solution studies revealed that the introduction of the methylene spacer between the imine moiety and the terminal phenyl moieties dramatically change the spatial orientation of the phenyl moieties. The signals of the phenyl moieties of the complex $\mathbf{3}_2\mathrm{Zn}^{2+}$ were overall strongly shielded ($\Delta\delta = 1.0$) with respect to the ligand **3**, suggesting strong intramolecular attractive $\pi-\pi$ stacking interactions between the phenyl and central pyridine moieties.

The unit cell of the complex $\mathbf{3}_2\mathrm{Zn}^{2+}$ was found to contain four duplex complexes together with eight triflate counterions. In the crystal the two ligands are strongly intertwined stabilising the duplex superstructure by internal $\pi-\pi$ stacking interactions (Figure 2(c)). The relative position of the duplex ligands allows an internal overlap between the phenyl moieties and the central pyridine moiety with an average centroid–centroid distance of 3.9 Å corresponding to a van der Waals contact. In the crystal, the communication between duplexes $\mathbf{3}_2\mathrm{Zn}^{2+}$ is disrupted, each duplex being closely packed with the two neighbouring ones by weak van der Waals contacts (Figure 4). It is useful to briefly emphasise the influence of the introduction of the methylene spacer which is clearly important for internal holding and stabilising the duplex formation by the $\pi-\pi$ stacking. However, the external $\pi-\pi$ stacking communication is completely removed and non-communicating duplex

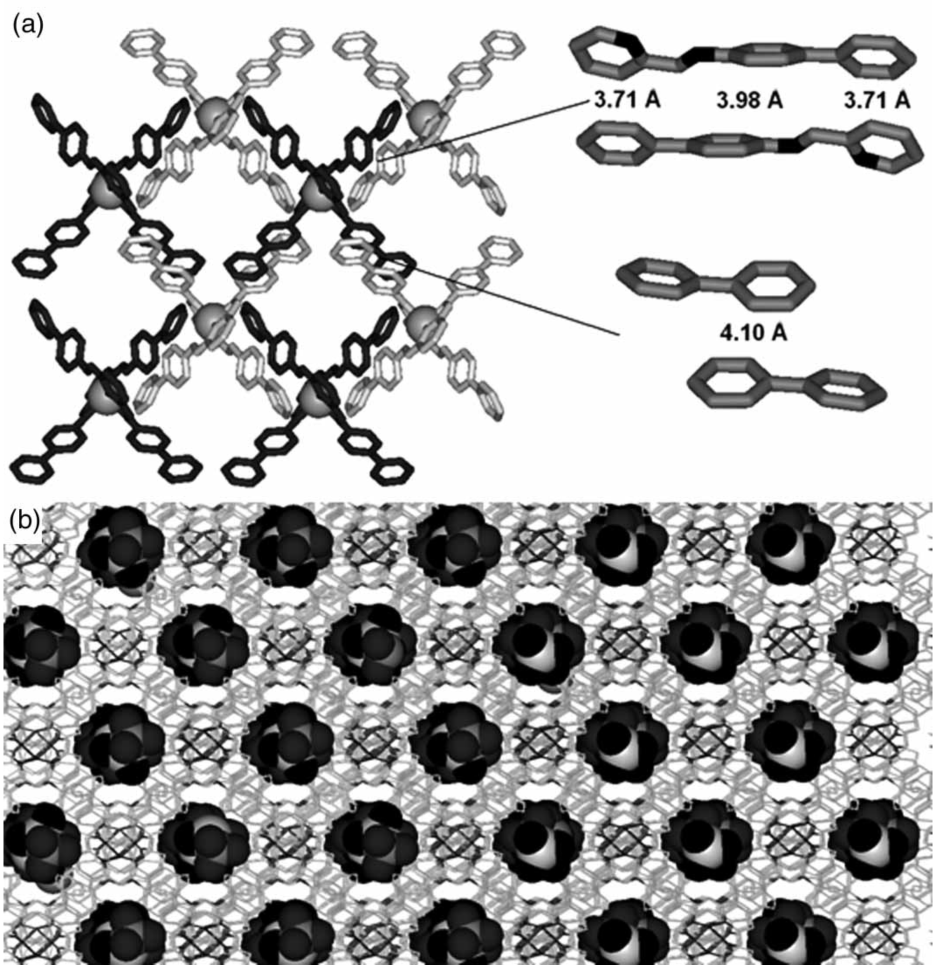


Figure 3. Crystal packing of the duplex complex $\mathbf{2}_2\mathrm{Zn}^{2+}$: (a) side view in stick representation and enlarged details of the $\pi-\pi$ stacking interactions, (b) the square packing arrangement of duplex subunits with the triflate anions in CPK representation filling the central cavity of the resulted tubular channels. The $\mathrm{Zn}^{2+}$ ions are shown as grey spheres.

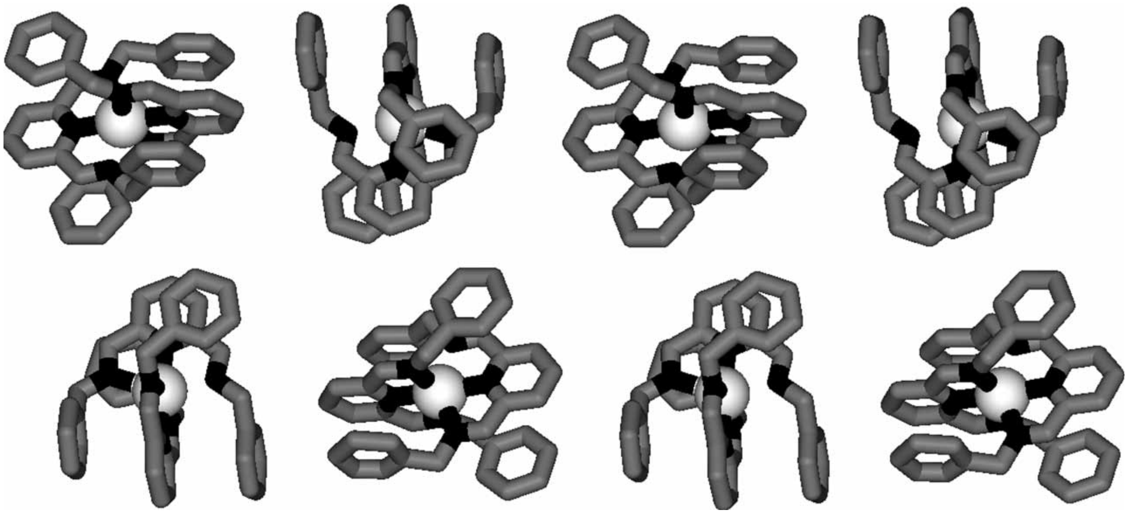


Figure 4. Crystal packing in stick representation of the duplex complex $\mathbf{3}_2\mathrm{Zn}^{2+}$.

structures are present in the crystal structure. Overall, the crystal structure is racemic and Δ and Λ mirror enantiomers duplexes are closely packed via van der Waals contacts.

Compared with $\mathbf{1}_2Zn^{2+}$ duplex with an intermediate orientation of the terminal phenyl rings allowing internal and external $\pi-\pi$ stacking interactions, the external aromatic interactions are completely suppressed in the $\mathbf{3}_2Zn^{2+}$ framework and further substitution of the methylene moiety in **3** with a second phenyl moiety in ligand **4** would result in external structural communication between the multi-aromatic duplexes $\mathbf{4}_2Zn^{2+}$.

The free rotation of the diphenylmethane groups around CH—N bond is possible in *cisoid–cisoid* (*5f*) conformation of the ligand **4** and one singlet was identified in $^1$H NMR spectrum. Two sets of singlet signals were identified in the regions of 7.9 and 5.5 ppm of $^1$H NMR spectrum of $\mathbf{4}_2Zn^{2+}$ for imine and CH protons, indicating a hindered rotation of the four diphenylmethane groups sterically very close to the neighbouring ones (Figure 2(d)) when $\mathbf{4}_2Zn^{2+}$ duplexes form in the presence of the $Zn^{2+}$ metal ions. On account of the hindered rotation of diphenylmethane groups around CH—N bond in the $\mathbf{4}_2Zn^{2+}$ duplex, the two sets of signals in the $^1$H NMR spectrum can be assigned to the Δ and Λ mirror atropenantiomers (Supporting Material, available online).

The unit cell of $\mathbf{4}_2Zn^{2+}$complex was found to contain 16 duplex complexes together with 32 very disordered triflate counterions and filling the interstices between the duplexes so that all available space is filled. Symmetry expansion of the crystal cell of $\mathbf{4}_2Zn^{2+}$shows that the self-assembly of the duplex units form triangle-like trimers. Three duplexes of the same chirality are self-assembled into a metallosupramolecular triangle that is stabilised by a new three-dimensional 'diphenylmethane embrace trimer' in which three V-shaped bisaromatic units fill their interstices so that their internal available space is filled (Figure 5(a)). Aromatic embrace motifs are well documented for a series of aromatic clusters (*10*) and their significance in terms of interactions (for example, stabilisation energy of the

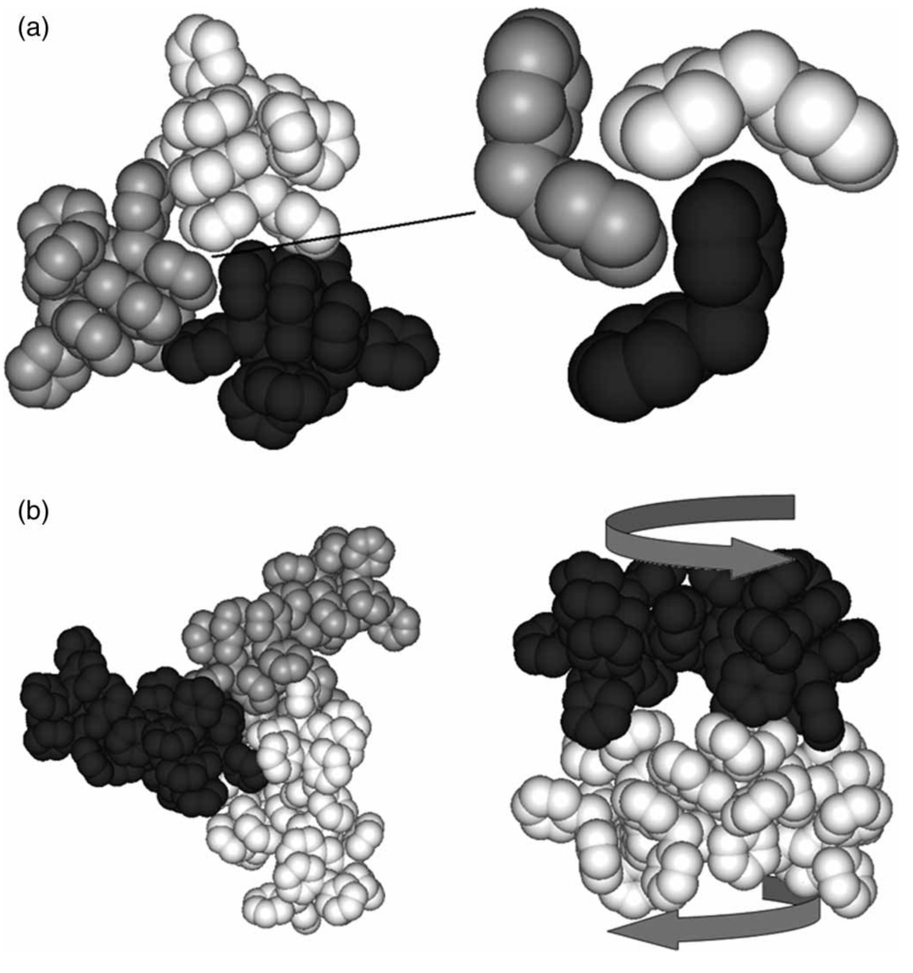


Figure 5. Crystal packing of the duplex complex $\mathbf{4}_2Zn^{2+}$: (a) side view in CPK representation of triangle like trimers and enlarged details of the 'diphenylmethane embrace motif'. (b) The packing arrangement of homochiral triangle enantiomers: top view of tetrahedral nodes and side view in CPK representation of face-to-face triangle self-assembly.

benzene trimer is estimated to be $-20\,\mathrm{kJ/mol}$) is widely recognised (*14*). Diphenylbenzene trimers formation in the solid state has been previously reported (*15*). The diphenylmethane embrace trimerisation in $\mathbf{4}_2\mathrm{Zn}^{2+}$ may contribute to the stabilisation of such hierarchically self-assembled duplexes. The crystal structure is racemic. The homochiral triangles connected via tetrahedral nodes and face-to-face triangle interactions are organised in the crystal that each duplex constituent has an alternative opposite chirality (Figure 5(b)).

## Conclusion

In conclusion, we have demonstrated in this paper the synthesis of large solid-state supramolecular crystalline superstructures stitched together from a combination of metal coordination and weak $\pi-\pi$ stacking and van der Waals aromatic interactions. Hierarchical supramolecular organisation is promoted by the formation of metallosupramolecular duplex architectures stabilised by internal $\pi-\pi$ stacking interactions and by long-range supramolecular spatial interactions between duplex systems via specific aromatic interactions. Long-range three-dimensional supramolecular structure propagation is favoured via weak internal stacking interactions towards robust double-helical configurations in $\mathbf{1}_2\mathrm{Zn}^{2+}$, tubular squared packed architecture in $\mathbf{2}_2\mathrm{Zn}^{2+}$ and homochiral triangles in $\mathbf{4}_2\mathrm{Zn}^{2+}$. The advantageous structural features of such external interactions are not preserved while introducing new variables such as methylene spacer between imine moiety and phenyl groups, inducing a very different spatial orientation of the lateral aromatic arms in $\mathbf{3}_2\mathrm{Zn}^{2+}$. This configuration is clearly important for internal holding and stabilise the duplex formation by the $\pi-\pi$ stacking. However, the external $\pi-\pi$ stacking interactions are completely removed and non-communicating duplex structures are present in the crystal structure of $\mathbf{3}_2\mathrm{Zn}^{2+}$. Indeed, the introduction of supplementary aromatic functionality results in the combination of both internal and external forces and has led to metallosupramolecular triangle architectures that are stabilised by a new three-dimensional 'diphenylmethane embrace motif'.

The use of such multiple hierarchical aromatic interactions provides a very powerful tool and a target supramolecular platform for the stabilisation of constitutional tertiary superstructures but also for a kind of modulable structure in the presence of external stimuli. Functional supramolecular devices for gas storage or catalysts are envisaged for the systems reported here and such studies are underway.

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