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Metallosupramolecular Architectures of Pseudoterpyridine-Type Ligands and Zn^{II} Metal Ions

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ABSTRACT: This paper reports the solid state structures of two new metallosupramolecular complexes resulting from pseudoterpyridine bis-hydrazone-type **3** and bis-acylhydrazone-type **4** ligands and Zn^{II} metal ions. The complex **3**₂Zn^{II} are quantitatively trapped by crystallization via constitutionally driven selection from binary solutions of 1:1 and 2:1 **3**:Zn^{II} (mol: mol). The constitutional internal overlap between the phenyl moieties and the central pyridine moiety clearly plays an important role for internal holding and stabilizing the duplex formation by $\pi-\pi$ stacking. The crystal **4**Zn^{II}***4** heterostructure and its packing reported in this paper present uncommon features with many other similar architectures reported by now. This structure shows a relatively new structural concept: the **4**Zn^{II} complex in which the Zn^{II} ions are coordinated by one ligand rolling the axial position of the metal ion, further interacting by H-bonding with the free ligand **4** in the crystal, allowing one to obtain 2D-layered architectures.

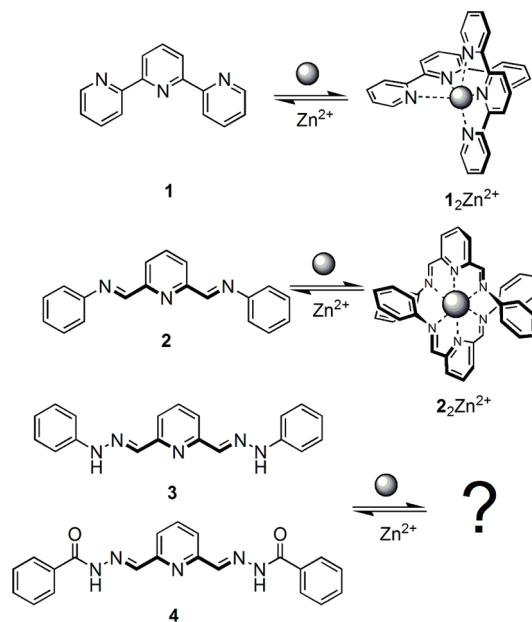
Introduction

The design and construction of metallosupramolecular architectures has attracted intense interest not only for their potential applications as new functional materials but also for their fascinating structural diversity.¹ Self-organization of such entities may be directed by design and is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry.²

The design of the ligand is crucial and bipyridine-, terpyridine- or polypyridine-type derivatives are extensively used.³ Their synthesis is very challenging, and laborious synthetic procedures for building up such ligands are needed.⁴ The isomorphic correspondence between terpyridine (terpy), **1**, and 2,6-(iminoarene)pyridine compound, **2**, provides a solution for greatly facilitating the synthetic procedure by replacing the formation of heterocyclic synthesis with simple imino-condensation reactions.⁵ Imine generation and exchange has been extensively used for designing dynamic adaptive systems. It provides a more direct access to complex systems which are useful building blocks for the generation of grids,^{5a} dynamic double helices,^{5b–e} borromean rings,^{2b} catenanes and rotaxanes^{5f} etc. In this context we have shown previously that the addition of Zn^{II} to the terpy-type ligand **2** causes the appropriate recruitment of two ligands in a pairwise mode^{5c} (Scheme 1, Figure 1a). In the crystal of **2**₂Zn^{II} each duplex of one one chirality (Δ or Λ) is $\pi-\pi$ stacked with two duplexes of the same chirality. This pattern generates double helix stacks of **2**₂Zn^{II} units of one handedness (Figure 2a).

Further developments might consider hydrazone or acylhydrazone functionalities providing both dynamic characters

Scheme 1. Structures of the Terpyridine-Type Ligands 1–4 and of the 1₂Zn^{II} and 2₂Zn^{II} Metallosupramolecular Complexes



through the reversibility of the imino bond and may introduce additional coordination, H-bonding and geometrical behaviors in the organization of metallosupramolecular architectures through the secondary amine and amide groups. The aim of this paper is to show how the coordination to a metallic center and the supramolecular packing of bis-chelate metal complexes **3**₂Zn^{II} and **4**₂Zn^{II} can be influenced by introducing secondary amino ($-NH-$) and acyl ($-NH-CO-$) spacers in the structure of new ligands **3** and **4**. In the next step, it is also of interest to investigate whether such changes of structural information of the ligand considering *inner* (related to coordination behavior around the metal ion) and *outer* (related to further supramolecular interaction within crystal) *structural factors* can modulate the coordination behavior

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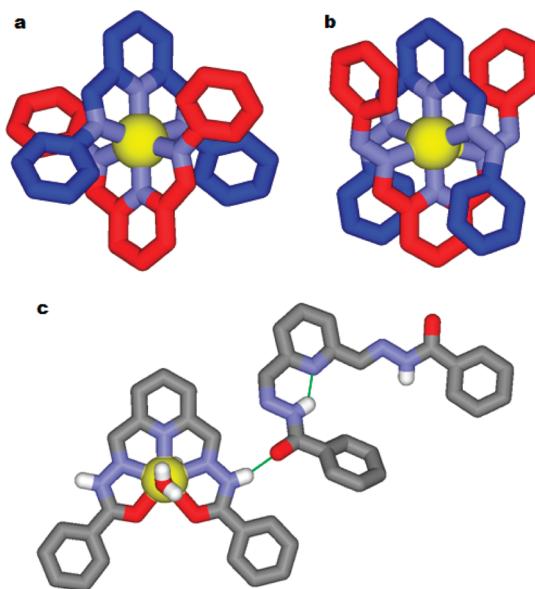


Figure 1. Crystal structure in stick representation of the complexes (a) 2Zn^{II} , (b) 3_2Zn^{II} and (c) H-bonding self-assembly of mononuclear complex 4Zn^{II} and the free ligand **3** in the crystal. The Zn^{II} ions are shown as yellow spheres.

around the metal ion or the expression of the crystal packing of resulted architectures.

Results and Discussion

Ligands Design and Synthesis. For all these reasons, in this study, the terpyridine-type (terpy) ligands like the 2,6-(phenylhydrazone)pyridine **3** and 2,6-(phenylacetylhydrazone)pyridine **4** compounds, giving easy synthetic access to new coordination systems, will be investigated (Scheme 1). We describe the synthesis of the ligands **3** and **4** and their corresponding Zn^{II} complexes. We report the crystal structures of such complexes which assemble into complementary bis-chelate compound 3_2Zn^{II} and self-associated architecture $4\text{Zn}^{\text{II}}*\mathbf{4}$. Ligands **3** and **4** have been synthesized in EtOH by condensation of one equivalent of 2,6-pyridinedicarboxaldehyde with two equivalents of phenylhydrazone and phenylacetylhydrazone, respectively. The solutions of **3** and of **4** in $\text{DMSO}-d_6$ give the sharp ^1H NMR spectra with a strong deshielding of meta protons of the central pyridine, consistent with the *transoid* conformation of the $-\text{N}=\text{C}-\text{C}=\text{N}-$ moiety; this effect agrees with an unwrapped conformation of compounds **3** and **4**.^{4g} The 3_2Zn^{II} and $4\text{Zn}^{\text{II}}*\mathbf{4}$ complexes were synthesized in CD_3CN (1 mL) by mixing 24 h at $60\ ^\circ\text{C}$ $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and ligands **3** ($\text{Zn}^{\text{II}}:\mathbf{3}$, 1:2 and 1:1, mol: mol) and **4** ($\text{Zn}^{\text{II}}:\mathbf{4}$, 1:2 and 1:1, mol: mol). The crystal structures of the complexes 3_2Zn^{II} and $4\text{Zn}^{\text{II}}*\mathbf{4}$ were determined from crystals obtained from the acetonitrile/isopropyl ether solutions at room temperature. The molecular and the crystal packing structures are presented in Figures 1 and 2.

Solid State Structures of the 3_2Zn^{II} and $4\text{Zn}^{\text{II}}*\mathbf{4}$ Complexes. The unit cell of 3_2Zn^{II} was found to contain eight complexes together with sixteen triflate counterions. As expected, the solution studies revealed that the introduction of the NH spacer between the imine moiety and the terminal phenyl moieties dramatically change the spatial orientation of the phenyl moieties, in a similar manner like the isomorphous zinc complex of 2,6-(benzylimino)pyridine^{5g} and copper complex of 2,6-(4-carboxybenzylimino)pyridine⁷ ligands. In the ^1H NMR spectrum the signals of the phenyl moieties of the complex 3_2Zn^{II} were

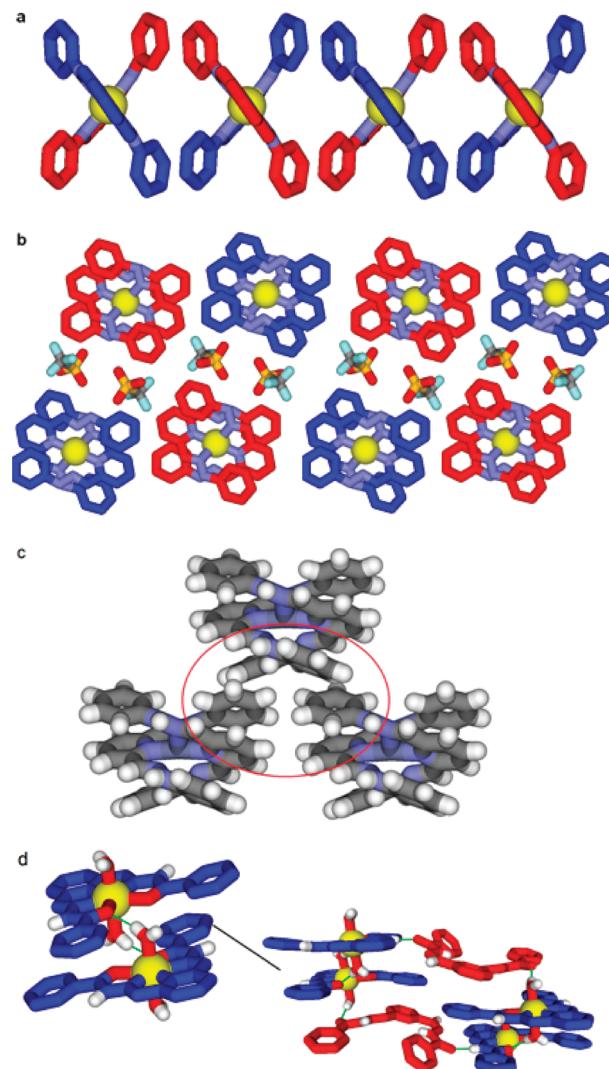


Figure 2. Side view in stick representation of the crystal packing of the complexes (a) 2Zn^{II} , (b) 3_2Zn^{II} , (c) edge-to-face (EF) embrace motif between phenyl groups of three 3_2Zn^{II} complexes and (d) H-bonding self-assembly of mononuclear complex 4Zn^{II} and free ligand **4**. The Zn^{II} ions are shown as yellow spheres. The blue and red colors have been used for clarity.

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 moiety. In the crystal the two ligands are strongly intertwined stabilizing the duplex superstructure by internal $\pi-\pi$ stacking interactions (Figure 1b). Moreover, the duplex 3_2Zn^{II} is still present in solution on further excess addition of Zn^{II} ions (maximum addition performed 4.5 equiv). In the duplex structure 3_2Zn^{II} the Zn^{II} ions are fully coordinated by two ligands arranged into two angular (72°) planes and present a distorted octahedral coordination geometry. The average $\text{Zn}^{\text{II}}-\text{N}_{\text{Pyridine}}$ and $\text{Zn}^{\text{II}}-\text{N}_{\text{imine}}$ distances are 1.99 or 2.27 Å, respectively. 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 distances of 3.6–3.8 Å corresponding to a $\pi-\pi$ stacking contact. In the crystal the duplexes 3_2Zn^{II} are not interacting so that each duplex is closely packed with the two neighboring ones by a flattened edge to face (EF) embrace motif (Figures 2b,c and 3b). It is useful to briefly emphasize the influence of the introduction of the NH (i.e., similar to methylene CH^{5g}) spacer which is clearly important

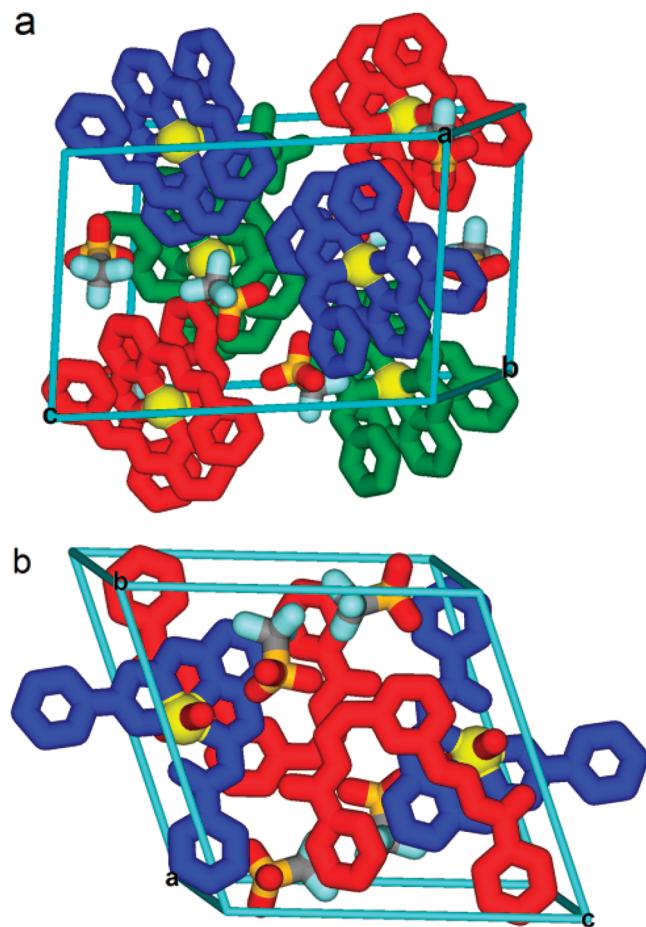


Figure 3. Crystal packing of the complexes (a) 3_2Zn^{II} and (b) H-bonding self-assembly of mononuclear complex 4Zn^{II} and free ligand **4**. The Zn^{II} ions are shown as yellow spheres. The blue, red, and green colors have been used for clarity.

for internal holding and stabilizing the duplex formation by the $\pi-\pi$ stacking. However the external $\pi-\pi$ stacking “communication” observed in the case of 2_2Zn^{II} complex is completely removed and “noncommunicating” duplex structures of 3_2Zn^{II} are present in the crystal structure. Attempts to crystallize the monoligand complex 3Zn^{II} failed, proving the nice stability of duplex structures 3_2Zn^{II} , and only nice red monocrystals of the duplex, with no formation of any other solid phase, can be obtained from stoichiometric binary mixtures (1:1, mol:mol) of different solution-diffusion experiments. Overall the crystal structure is racemic and Δ and Λ mirror enantiomer duplexes are closely packed in one direction, into parallel layers which are alternatively stratified. Two triflate anions are connecting two duplex structures via H-bonding to NH groups (average distance of 2.07 Å) and filling the interstices so that all available space is filled (Figures 2b, 3a).

In the ^1H NMR spectrum of a solution of $4:\text{Zn}^{\text{II}}$, 2:1 mol: mol mixture in acetonitrile we observe the formation of the monoligand complex 4Zn^{II} (as confirmed by the spectrum of 1:1 solution). The peaks of the $4:\text{Zn}^{\text{II}}$, 2:1 mixture sharpened indicating rapid equilibration of 4Zn^{II} with the free ligand on the NMR time scale. Further, layering a solution of $4:\text{Zn}^{\text{II}}$, 2:1 mol:mol mixture in acetonitrile with the isopropyl ether resulted in a unique set of crystals of $4\text{Zn}^{\text{II}}*\mathbf{4}$ containing the monoligand complex 4Zn^{II} associated with the uncomplexed ligand molecule **4** by H-bonding (Figure 1c). The unit cell was found to contain two 4Zn^{II} complexes and two ligand **4** molecules together with four water molecules and four triflate

counterions. As observed from the solution studies the formation of monoligand 4Zn^{II} complex is almost quantitative at $4:\text{Zn}^{\text{II}}$, 2:1 mol:mol stoichiometry as shown by ^1H NMR and ESI-MS analysis. X-ray diffraction analysis confirms its structure as the zinc monoligand complex 4Zn^{II} with a coordination number of seven for the central zinc ion. The three nitrogen atoms of the pyridine system (average $\text{Zn}^{\text{II}}-\text{N}$ distances are all equal: 2.23 Å) and the two carbonyl oxygen atoms (average $\text{Zn}^{\text{II}}-\text{O}$ distance is 2.25 Å) complex the metal ion in a circular fashion, whereas two water molecules lie perpendicular (average $\text{Zn}^{\text{II}}-\text{O}$ distance is 2.06 Å), thereby forming a distorted pentagonal bipyramid (Figures 1c, 2d, 3c). This coordination behavior may be explained by the extra coordination provided by the two carbonyl functions, sterically fitting the circular coordination geometry around the metal ion and which prevent the formation of an 4_2Zn^{II} -type complex. Similar structural data have been obtained very recently by Ulrich and Lehn⁸ for lead and zinc macrocycles resulting from rigid complex dialdehydes. The uncomplexed ligand **4** presents a half-folded conformation stabilized by a strong H-bond between the NH and pyridine moieties (average $-\text{NH}-\text{N}$ distance is 1.98 Å). Symmetry expansion of the crystal cell of $4\text{Zn}^{\text{II}}*\mathbf{4}$ shows that the self-assembly of the monocomplex 4Zn^{II} units form H-bonded dimers (Figure 2d). Two 4Zn^{II} units of the complex are self-assembled via two H-bonds between the coordinated water molecules and the carbonyl moieties of a vicinal complex (average $-\text{OH}\cdots\text{O}$ distance is 1.93 Å). Further the metallodimers are connected to free ligand molecules via $\text{N}-\text{H}\cdots\text{carbonyl}$ (average $-\text{NH}-\text{O}$ distance is 1.92 Å) and coordinated water–carbonyl (average $-\text{OH}\cdots\text{O}$ distance is 2.04 Å) H-bonds. Each dimer 4Zn^{II} associates in the crystal lattice via two ligand **4** bridges, forming parallel layers which are alternatively stratified (Figure 2d). The triflate anions are connecting such layered structures via H-bonding to NH groups (average distance of 1.92 Å) and filling the interstices so that all available space is filled. Unfortunately, until now, we cannot grow single crystals of 4Zn^{II} from a solution of $4:\text{Zn}^{\text{II}}$, 1:1 mol:mol.

Conclusion

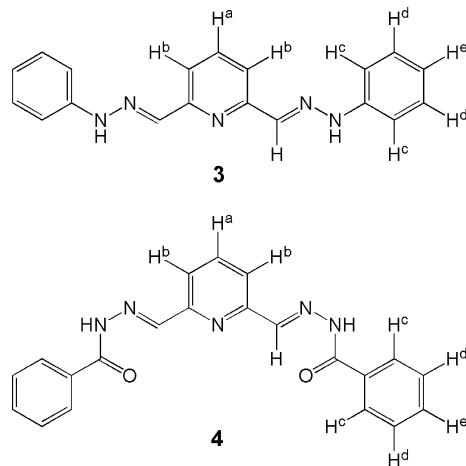
In conclusion the present results report the solid state structures of two complexes resulting from terpyridine-type ligands **3** and **4** and Zn^{II} metal ions. The complexes 3_2Zn^{II} are quantitatively trapped by crystallization via constitutionally driven selection from binary solutions of 1:1 and 2:1 $3:\text{Zn}^{\text{II}}$ (mol:mol). The constitutional internal overlap between the phenyl moieties and the central pyridine moiety clearly plays an important role for internal holding and stabilizing the duplex formation by the $\pi-\pi$ stacking. The crystal $4\text{Zn}^{\text{II}}*\mathbf{4}$ heterostructure and its packing reported in this paper present uncommon features with many other similar architectures reported by now.⁵ This structure shows a relatively new structural concept: the 4Zn^{II} complex in which the Zn^{II} ions are coordinated by one ligand rolling the axial position of the metal ion further interacts by H-bonding with the free ligand **4** in the crystal, allowing one to obtain 2D-layered architectures.⁸

A further step toward such more complex systems could involve side-by-side formation of “dynamic ligands” by correct selection of their specific components by reversible interconnections. We are currently extending this approach

to such optical, magnetic, etc. dynamic combinatorial nanosystems.

Experimental Section

Materials and Methods. 2,6-Pyridinedicarboxaldehyde was prepared by oxidation of 2,6-pyridinemethanol with activated MnO₂ according to the procedure described in the literature.^{5b} 4-Phenylhydrazone and phenylacetylhydrazone were purchased from Aldrich 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 sulfate (Na₂SO₄). ¹H and ¹³C NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in DMSO-*d*₆, DMSO-*d*₆/CDCl₃ and CD₃CN with the use of the residual solvent peak as reference. 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 Ligand 3. **3** has been synthesized in EtOH by condensation of 2,6-pyridine dicarboxaldehyde (0.1 g, 0.74 mmol) with phenylhydrazone (0.159 g, 1.48 mmol), under reflux for 12 h with constant stirring. After solvent evaporation, the resulting crude material was recrystallized from acetonitrile to give **3** as a red-yellow solid, (0.275 g, 85%). C₁₉H₁₇N₅: MW = 315.38 g/mol; ¹H NMR (300 MHz, CDCl₃/DMSO-*d*₆, ppm) δ = 9.611 (s, 2H, NH), 7.823 (s, 2H, CH=N), 7.775–7.749 (d, 2H, H^b, *J* = 7.8 Hz), 7.620–7.569 (t, 1H, H^a, *J* = 7.5 Hz, *J* = 7.8 Hz), 7.181–7.157 (d, 4H, H^c, *J* = 7.2 Hz), 7.111–7.087 (d, 4H, H^d, *J* = 7.2 Hz), 6.789–6.765 (t, 2H, H^e, *J* = 7.2 Hz); ¹³C NMR (CDCl₃/DMSO-*d*₆, ppm) δ = 161.83, 144.23, 135.8, 128.62, 119.44, 117.25, 112.33; MS (ESI) *m/z* (%) 316.6 (100) [3 – H]⁺.

Synthesis of Ligand 4. **4** has been synthesized in EtOH by condensation of 2,6-pyridine dicarboxaldehyde (0.1 g, 0.74 mmol) with phenylacetylhydrazone (0.201 g, 1.48 mmol), under reflux for 12 h with constant stirring. After solvent evaporation, the resulting crude material was recrystallized from acetonitrile to give **4** as a white solid (0.247 g, 90%). C₂₁H₁₇N₅O₂: MW = 371.40 g/mol; ¹H NMR (300 MHz, DMSO-*d*₆, ppm) δ = 12.1 (s, 1H, NHCO), 12.3 (s, 1H, NH), 8.527 (s, 2H, CH=N), 7.995–7.929 (m, 2H, H^b), 7.86–7.835 (d, 1H, H^a), 7.668–7.535 (m, 10H, H^{c,d,e}); ¹³C NMR (DMSO-*d*₆, ppm) δ = 161.84, 153.27, 128.54, 127.68; MS (ESI) *m/z* (%) 372.7 (100) [4 – H]⁺.

Synthesis and Single Crystal Structures of 3₂Zn^{II}–4Zn^{II}*4 Complexes. The reactions were performed typically on a 10 mg scale of ligand. The ligands **3** and **4** and Zn(CF₃SO₃)₂ (molar ratio ligand–metal 2:1) were dissolved in CD₃CN (1 mL), and stirred overnight at 60 °C. These solutions were monitored by ¹H NMR and ESI mass spectrometries. Layering such solutions of duplex complexes 3₂Zn^{II}–4₂Zn^{II} in acetonitrile with isopropyl ether at room temperature resulted in a unique set of single crystals suitable for X-ray single-crystal experiments.

Complex 3₂Zn^{II}. Red crystals: ¹H NMR (300 MHz, CD₃CN, ppm) δ = 9.895 (s, 4H, NH), 7.844 (s, 4H, CH=N), 7.619–7.567 (t, 2H,

H^a, *J* = 7.8 Hz), 7.013–6.986 (d, 4H, H^b, *J* = 8.1 Hz), 6.917–6.820 (m, 16H, H^c + H^d), 6.740–6.689 (m, 4H, H^e); ¹³C NMR (300 MHz, CD₃CN, ppm) δ = 162.33, 147.46, 142.75, 140.53, 135.89, 128.64, 124.12, 123.85, 116.98, 116.74; MS (ESI) *m/z* (%) 348.4 (100) [Zn(3)₂]^{II}.

Complex 4₂Zn^{II}. White crystals: ¹H NMR (300 MHz, CD₃CN, ppm) δ = 12.318 (b, 2H, NH), 8.634 (s, 2H, CH=N), 8.352–8.300 (t, 1H, H^a, *J* = 8.1 Hz, 7.5 Hz), 8.160–8.132 (d, 4H, H^c, *J* = 7.2 Hz), 8.022–7.996 (d, 2H, H^b, *J* = 7.8 Hz), 7.836–7.782 (t, 2H, H^e, *J* = 7.5 Hz), 7.718–7.668 (t, 4H, H^d, *J* = 7.8 Hz, 7.2 Hz); MS (ESI) *m/z* (%) 588.8 (100) [Zn(4)₂]^{II}(CF₃SO₃)⁻, 403.4 (100) [Zn(4)₂]^{II}, [Zn(4)]^{II*}(4), 588.8 (90) {[Zn(4)](CF₃SO₃)^{+3SO₃)⁺(4)} or {[Zn(4)₂]•(CF₃SO₃)⁺}.}

X-ray Single Crystal Diffraction Data for 3₂Zn^{II} and 4Zn^{II}*4 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^{6a} or by ab initio (charge-flipping) methods using SUPERFLIP^{6b} and refined by least-squares methods on *F* using CRYSTALS,^{6c} against |*F*| on data having *I* > 2σ(*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 ratio did not allow doing this. Full details can be found in the cif files.

Single Crystals of 3₂Zn^{II}. Single crystals of 3₂Zn^{II}, C₈₀H₃₀F₁₂N₁₆O₁₆S₄Zn₂, were grown from acetonitrile/isopropyl ether. A single red transparent crystal of dimension 0.20 × 0.22 × 0.24 mm was selected. Unit cell monoclinic, space group *C*12/c1, cell dimensions: *a* = 13.3943(3) Å, *b* = 16.2129(4) Å, *c* = 19.7183(5) Å, α = γ = 90°, β = 96.844(2)° *V* = 4251.52(18) Å³, *Z* = 4, *M_r* = 994.3, ρ = 1.553 g cm⁻³, θ_{\max} = 32.519°, *N_{ref}(tot)* = 30243, *N_{ref}(unique)*, *I* > 2σ(*I*) = 1884; *N_{par}* = 242, *R*₁ = 0.0587, and *wR*₂ = 0.0526.

Single Crystals of 4Zn^{II}*4. Single crystals of 4Zn^{II}*4, C₄₄H₄₀F₆N₁₀O₁₃S₂Zn, were grown from acetonitrile/isopropyl ether. A single yellow transparent crystal of dimension 0.17 × 0.25 × 0.38 mm was selected. Unit cell triclinic, space group *P*1̄, cell dimensions: *a* = 11.0531(8) Å, *b* = 15.7333(9) Å, *c* = 15.8447(1) Å, α = 106.704°, β = 106.742°, γ = 96.247°, *V* = 2471.5(3) Å³, *Z* = 2, *M_r* = 1160.36, ρ = 1.55 g cm⁻³, θ_{\max} = 21.32°, *N_{ref}(tot)* = 14224, *N_{ref}(unique)*, *I* > 2σ(*I*) = 8669; *N_{par}* = 304, *R*₁ = 0.03472, and *wR*₂ = 0.0512.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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