Homo- and Heteroduplex Complexes Containing Terpyridine-Type Ligands and Zn^{2+}

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We describe a study of the equilibrium binding of Zn^{2+} to binary mixtures of tridentate terpy-type ligands **1**–**3**, which leads to the formation of a dynamic mixture of homo (**4**–**6**) and hetero (**7**–**9**) coordination compounds. We report the crystal structures of five such complexes (**4**, **5**, **7**–**9**) which assemble into complementary duplex compounds that further self-organize into double helical- or lamellar-type architectures in the solid state. The ligand exchange between homoduplex complexes in solution leads to the preferential formation of the heteroduplex complexes. As might be expected, these processes display a statistical distribution of homoduplex:heteroduplex:homoduplex complexes of 1:2:1 for the mixtures resulting from **4**:**6** and **5**:**6** ligands. However, complex **8** is preferred in a **4**:**5** mixture which presents a composition of 1:4:1 (amplification factor of about 33 %). The X-ray structural determinations of selected single crystals resulting from the stoichiometric mixtures of homoduplex complexes show unique heteroduplex superstructures **7**–**9** in the solid state. The present results present the solid-state structures of homo- and heterocomplexes resulting from terpyridine-type ligands **1**–**3** and Zn^{2+} metal ions. The heteroduplex Zn^{2+} complexes **7**–**9** are quantitatively crystallized in the solid state by statistical (**7**, **9**) and structural (**8**) driven selection in solution from a binary mixture of the terpyridine-type complexes and then trapped by crystallization in the solid state.

Introduction

Under biological and environmental conditions, multiligand-multimetal equilibria dominate homonuclear interactions and mixed- or higher-order complexes are formed.[1] Thus it becomes understandable why the mixed complexes have been studied extensively during the last four decades. The most simple of these species − the ternary (heteroduplex) complexes − consist of a metal ion and two different ligands. The driving forces leading to the formation of such complexes are statistical events, and non-covalent forces like charge and hydrophobic or π-π stacking interactions.[2]

The self-organization of metallosupramolecular 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. The design of the ligand is crucial, and bipyridine, terpyridine, etc. derivatives have been extensively used.[3] The synthesis of such ligands is very challenging and other simple procedures are much sought-after as they may provide a more direct access to these systems by using or imine and hydrazone mimics, which are useful building blocks for the generation of grid-type, cage, helical architectures, etc.[4–7]

Coordination complexes based on terpyridine-type ligands **1** and octahedrally coordinated metal ions are of special interest as they reveal a range of interesting structural and physicochemical properties.[5] Other terpyridine-type (terpy) tridentate ligands like the bis-Schiff-base **2**[6] and the hydrazone bis-pyridine **3**[7] give easy synthetic access to similar systems (Scheme 1). Addition of Zn^{2+} to the binary mixture of terpy-type ligands **1**–**3** should cause the appropriate recruitment of two ligands in a pairwise mode and might be controlled by the coordination behavior and internal interactions between different aromatic moieties of these compounds. Specifically, it is of interest to investigate whether the coordination behavior of these systems on the addition of octahedral Zn^{2+} ions can be selectively expressed in the formation of ternary complexes.

We describe in this paper a study of the equilibrium binding of Zn^{2+} to binary mixtures of tridentate terpy-type ligands **1**–**3**, which leads to the formation of a dynamic mixture of homo- (**4**–**6**) and hetero- (**7**–**9**) coordination compounds. We report the crystal structures of five such complexes (**4**, **5**, **7**–**9**), which assemble into complementary duplex compounds that further self-organize into double helical- or lamellar-type architectures in the solid state.

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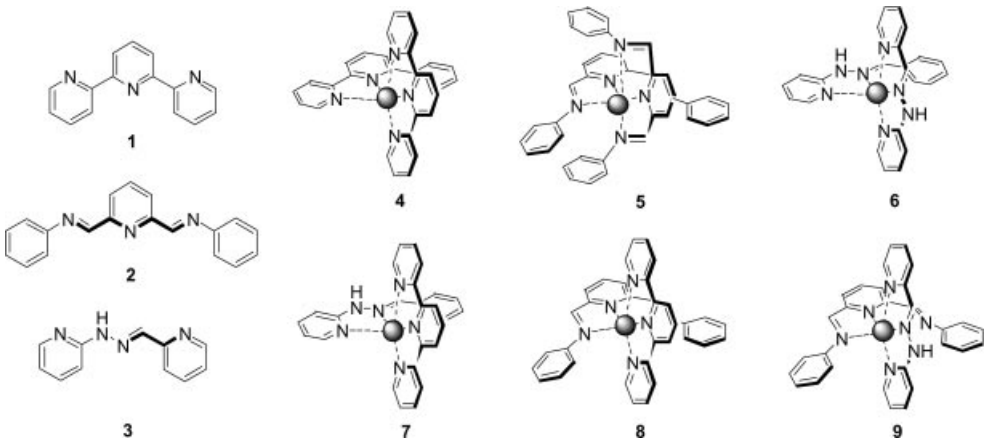


Scheme 1. Structures of the terpyridine-type ligands **1**–**3** and the combinatorial library of resulting homo- (**4**–**6**) and heteroduplex (**7**–**9**) metallosupramolecular complexes.

Result and Discussions

Synthesis and Characterization of Ligands 2 and 3

Ligands **2** and **3** were synthesized in EtOH by condensation of one equivalent of 2,6-pyridinedicarboxaldehyde with two equivalents of aniline and of one equivalent of 2-pyridinecarboxaldehyde with one equivalent of hydrazinopyridine, respectively. The solutions of **2** and of **3** in $CDCl_3$ give sharp ^1H NMR spectra with a strong deshielding of the *meta* protons of the central pyridine (**2**) and of the iminopyridine (**3**) rings, consistent with the *transoid* conformation[8] of the –N=C–C=N– moiety. As expected, a strong deshielding is observed for the *meta* pyridine hydrogens, thus indicating a tight contact with the neighboring imine nitrogen atoms; this effect agrees with an unwrapped conformation of compounds **2** and **3**.

Two-Component Self-Assembly, Generation and Interconversion of the Zn^{2+} Complexes Formed by Ligands 1–3

The formation of homoduplex Zn^{2+} complexes from terpyridine-type ligands **1**–**3** has been studied in detail because it is a very common prototype for coordination self-assembly processes and because of the physicochemical properties and functions that such materials may possess.[2–9] One may consider the formation of these complexes to result from the "reading" of the steric and binding information of the ligands by the Zn^{2+} ions following their octahedral coordination geometry.

Of particular interest, both as a control of the ligand selection and due to the formation of novel mixed species, would be the generation of the heteroduplex complexes from two different terpy-type ligands **1**–**3** and Zn^{2+} ions. Considering that Zn^{2+} ions, which display hexacoordination geometry, bind two terpy units in a octahedral geometry, one might expect that the exchange of different terpy-type ligands in the metal coordination sphere would result in the interconversion of all possible combinations. The rate of such exchange depends on the coordination behavior and on the specific interactions between ligands, therefore it should be possible to form mixtures from which a ternary architecture[10] can be amplified by favorable attractive interactions, including stacking[11] or hydrophobic[12] interactions, between the ligands, while minimizing the ligand–solvent interactions.[8]

As a step towards this goal, we decided to investigate the formation and interconversion of the Zn^{2+} duplex complexes that may result from the binding of Zn^{2+} ions to stoichiometric ratios (1:1) of binary mixtures of ligands **1**–**3**. Such systems form by self-assembly under mild conditions and are readily amenable to solution studies by ^1H NMR spectroscopy and ESI mass spectrometry.

The ^1H NMR spectra of homoduplex complexes **4**–**6** (Scheme 1) consist of a series of sharp peaks, indicating high symmetry (Figure 1). The spectra can be interpreted as ligands **1**–**3** in one magnetic environment and show a deshielding of the protons of the pyridine moieties due to the Zn^{2+} ion complexation. Tridentate metal ion coordination converts the *transoid* form of the free ligand to the *cisoid* one, corresponding to a terpy-type complexation site. The proton signals of the phenyl moieties of complex **5** are overall strongly shielded ($\Delta\delta$ = 0.5 ppm) with respect to ligand **2**, thus suggesting strong intramolecular attractive π-π stacking interactions between the phenyl and central pyri-

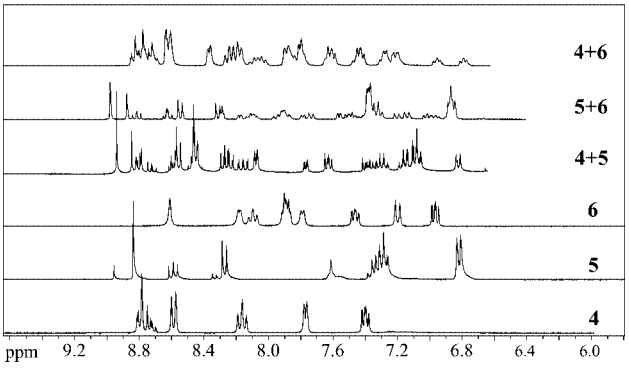


Figure 1. ^1H NMR spectra of the homoduplex complexes **4**–**6** in CD_3CN and of species resulting from the combination of stoichiometric binary mixtures of **4**:**5**, **5**:**6**, and **4**:**6** in a 1:1 molar ratio.

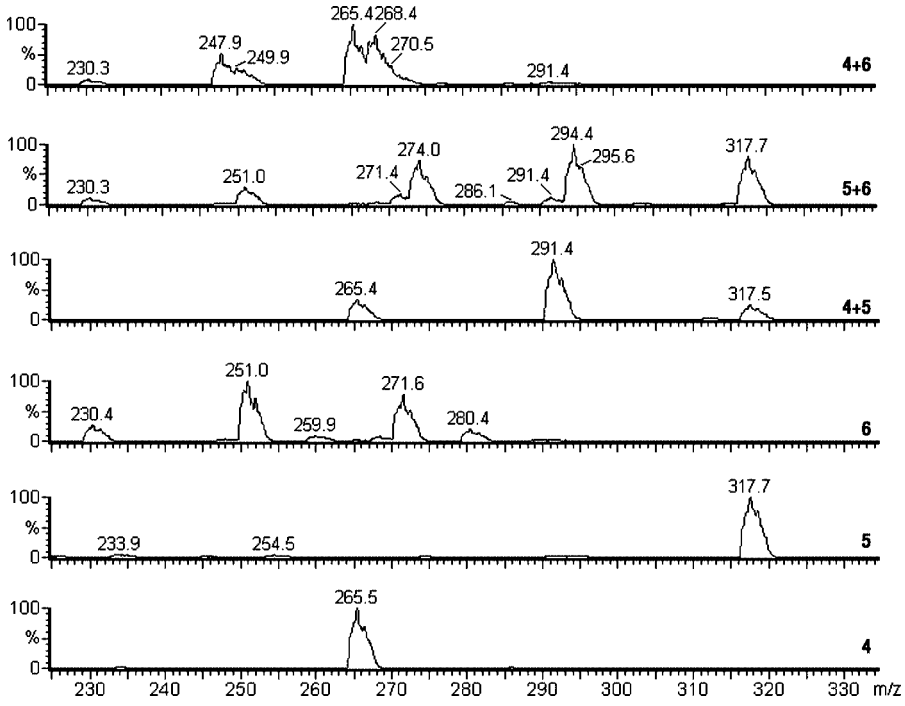


Figure 2. ESI mass spectra of the homoduplex complexes **4**–**6** in CH_3CN and of species resulting from the combination of stoichiometric binary mixtures of **4**:**5**, **5**:**6**, and **4**:**6** in a 1:1 molar ratio.

dine moiety. The ESI mass spectra of homoduplex Zn^{2+} complexes **4**–**6** show strong doubly charged molecular peaks at M/2 (**4**, **5**) or at (M + $n$$CH_3CN$)/2 ($n$ = 0–2, **6**; Figure 2).

The ligand exchange between Zn^{2+} complexes **4**–**6** was studied in the reaction of stoichiometric binary mixtures (**4**:**5**, **4**:**6**, **5**:**6**, 1:1, mol:mol) of homoduplex complexes. In all reactions the signals of symmetrical complexes as well as those of the cross-products were monitored by ^1H NMR spectroscopy (Figure 1) and ESI mass spectrometry (Figure 2). The same results were obtained by mixing two different ligands in a 1:1 ratio and by subsequently adding the stoichiometric amount of metal ions. The ^1H NMR spectra of the binary mixtures show three sets of sharp proton resonances and consist of the two initial homoduplex complexes together with the heteroduplex mixed species. We did not detect any N-exchange reaction between the bis-Schiff-base **2** and the hydrazone bis-pyridine **3** ligands; the core Zn^{2+}–ligand units, despite their kinetic lability, are thermodynamically very stable species in solution.

The ^1H NMR signals of heteroduplex complexes **7**–**9** show an overall shielding of the pyridine protons with respect to the homoduplex species, thereby suggesting an enhanced coordination power when two different ligands are coordinated. Moreover, the proton signals of the phenyl moieties of the heteroduplex complex **8** are overall strongly shielded ($\Delta\delta$ = 0.4 ppm) with respect to the homoduplex complex **5** (Figure 1). This suggests that intramolecular attractive π-π stacking interactions play an important role in the formation of the heteroduplex complexes **7**–**9**.

The ligand exchange was also monitored by ESI mass spectrometry; in all reactions, the mass spectra showed the preferential formation of the cross-products **7**–**9** after a rapid equilibration of the 1:1 solutions of the homoduplex complexes **4**–**6** (Figure 2). The composition of the binary mixtures was determined on the basis of the NMR signals of the imine, phenyl, and pyridine protons of the homo- and heteroduplex complexes **4**–**9**. As might be expected, these processes display a statistical distribution of homoduplex:heteroduplex:homoduplex complexes of 1:2:1 for the mixtures resulting from **4**:**6** and **5**:**6** ligands. However, complex **8** is preferred in a **4**:**5** mixture, which has a composition of 1:4:1. Considering the statistical distribution of 1:2:1 and the NMR detection limit error under the experimental conditions used is about 1%, the formation of **8** must display an amplification factor of about 33%.

Solid-State Structures of the Homoduplex (4, 5) and Heteroduplex (7–9) Zn^{2+} Complexes

The crystal structures of the complexes were determined from crystals obtained from acetonitrile/diisopropyl ether (**4**, **5**, **8**, **9**) and acetonitrile/benzene (**7**) solutions at room temperature. The molecular and the crystal packing structures are presented below. In all structures the Zn^{2+} ion is fully coordinated by two ligands and presents an octahedral coordination geometry. The average Zn^{2+}–$N_{Pyridine}$ Zn^{2+}–N_{imine}, and Zn^{2+}–$N_{hydrazone}$ distances are 2.07 or 2.20 (depending on the nature and the position of the pyridine moiety), 2.25, and 2.15 Å, respectively.

Surprisingly, only one crystal structure containing the $Zn(terpy)_2^{2+}$ [13a] duplex (with the peroxodisulfate counterion) was found in the Cambridge Structural Database (Feb-

ruary 2005).[13b] The unit cell of the new crystal structure of **4** was found to contain four homoduplex complexes together with eight triflate counterions. Each $Zn(terpy)_2^{2+}$ duplex has the two terpyridines arranged into two orthogonal planes (Figure 3a), associated by offset face-to-face (***off***)[5a] pyridine–pyridine interactions with average π-π stacking centroid–centroid distances of 3.90 Å.[12a] In the crystal lattice, the homoduplex cations of **4** pack in one direction into parallel layers that are alternatively stratified. In the adjacent layers, the terpyridine ligand planes on either side of the layer interface are rotated by 45° to each other (Figure 3b). The triflate anions and the cations are in van der Waals contact, thus disrupting the classical two-dimensional motif of "terpyridine embrace"[5a] and filling the interstices so that all available space is filled.

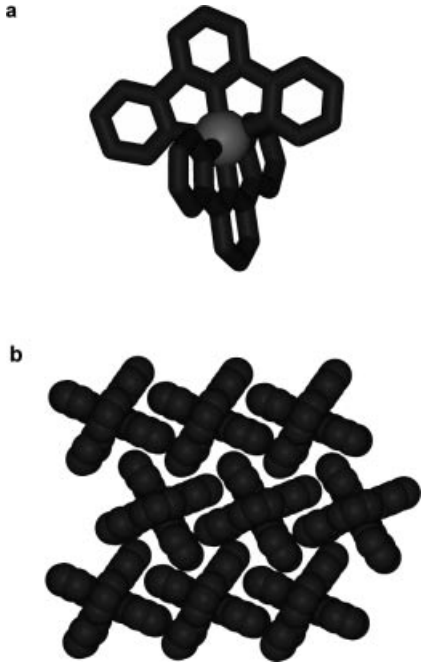


Figure 3. Crystal structure of the homoduplex complex **4**: a) side view in stick representation (the Zn^{2+} ion is shown as a gray sphere); b) space-filling representation of the crystal packing.

The unit cell of complex **5** was found to contain two homoduplex complexes together with four triflate counterions and four acetonitrile molecules. The two ligands of the duplex are arranged into two intertwined strands that are held together in double-helix form (0.5 turns per duplex) by the Zn^{2+} cation (Figure 4, a). As expected from the solution studies, the relative position of the duplex ligands allow an internal overlap between the phenyl moieties and the central pyridine moiety, with an average distance of 3.8 Å corresponding to a van der Waals contact. Each duplex of one helical sense is π-π stacked with two duplexes of the same helical sense (Figure 4, b). Each duplex present a tight contact with the two neighboring ones by stacking of the terminal phenyl moieties (average distance of 3.68 Å). This pattern generates infinite double helix stacks of units of one helical sense, with a helical pitch of about 15.3 Å. The crystal contains spontaneously resolved domains of alternate helicity. Accordingly, chiral double helical channels are generated in the solid state with an interior void of about 1.8 Å (considering a projection in a plane and taking into account the van der Waals radii of diagonally located N and C-H sites). The zinc ions are arranged into an approximately linear array that fits tightly into the central cavity of the double helical channel. The double helical entity is reminiscent of other terpyridine–Ag^+ complexes[5e] or of the double stranded dinuclear Ag^+ helicates[12b] described earlier.

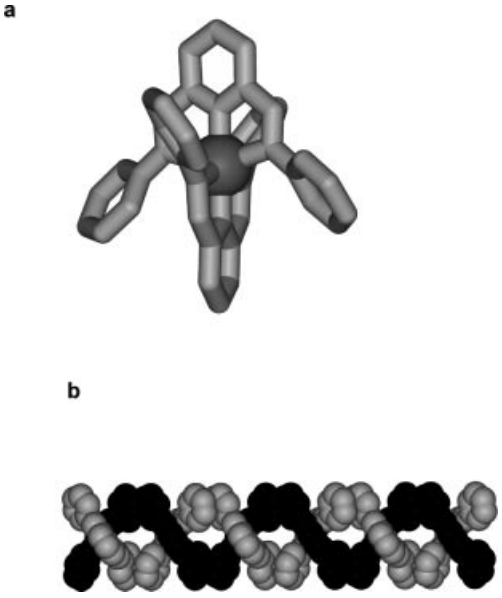


Figure 4. Crystal structure of the homoduplex complex **5**: a) side view in stick representation (the Zn^{2+} ion is shown as a gray sphere); b) space-filling representation of the crystal packing.

All attempts to crystallize complex **6** failed, and only tiny single crystals too small for X-ray analysis could be obtained from different solution-diffusion experiments.

Layering such solutions of stoichiometric binary mixtures (1:1, mol:mol) of homoduplex complexes **4**–**6** in acetonitrile with a non-solvent resulted in a unique set of crystals for each experiment. The X-ray structural determinations of selected single crystals resulting from these stoichiometric binary mixtures revealed that such complexes present unique heteroduplex superstructures **7**–**9** in the solid state. Redissolution of the crystals in CD_3CN results in regeneration of the reaction mixture prior to crystal growth. These features are similar to other dynamic processes operating in mixtures of coordination complexes from which a single member may be trapped by crystallization.[14]

The unit cell of complex **7** was found to contain four heteroduplex complexes together with eight triflate counterions and four benzene molecules. The two different ligands of the duplex are arranged into two orthogonal planes (Figure 5, a). Each duplex of **7** associates in the crystal lattice by terpyridine–terpyridine offset-face-to-face (***off***)[5a] interactions. They are restricted to one direction (average π-π stacking centroid–centroid distances of 3.75 Å), thus forming parallel layers that are alternatively stratified (Figure 5, b). Interactions in the other direction are disrupted, and the

hydrazone bis-pyridine ligands are not involved in pyridine–pyridine π-π stacking interactions (average centroid–centroid distances of 4.60 Å).

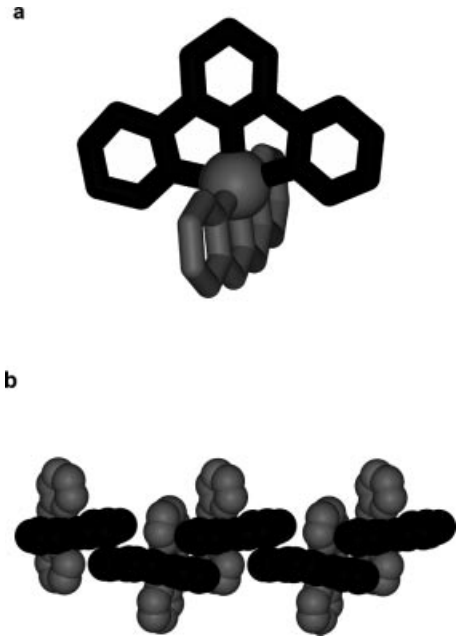


Figure 5. Crystal structure of the heteroduplex complex **7**: a) side view in stick representation (the Zn^{2+} ion is shown as a gray sphere); b) space-filling representation of the crystal packing.

The unit cell of complex **8** was found to contain four heteroduplex complexes together with eight triflate counterions and four acetonitrile molecules. The two different ligands of the duplex are arranged into two orthogonal planes (Figure 6, a). The relative flexibility of ligand **2** allows an internal overlap between the phenyl moieties and the central pyridine moiety of the terpyridine **1** with an average distance (3.98 Å) corresponding to a van der Waals contact. This is consistent with the NMR results and suggests that intramolecular attractive π-π stacking interactions play an important role in the preferential formation and amplification of the heteroduplex **8** from a stoichiometric mixture of **4** and **5**. Each heteroduplex of **8** associates two by two in the crystal lattice by terpyridine–terpyridine ***off*** interactions (average π-π stacking centroid–centroid distances of 3.75 Å), resulting in the formation of dimeric species that are alternatively stratified in the crystal lattice (Figure 6, b).

The unit cell of complex **9** was found to contain four heteroduplex complexes together with eight triflate counterions and four acetonitrile molecules. The two different ligands of the duplex are arranged into two orthogonal planes. The replacement of the central pyridine group by a hydrazone group in ligand **3** results in the disruption of the internal π-π stacking between the phenyl and pyridine moiety; in the heterocomplex **9** the phenyl substituents are perpendicularly twisted with the respect to the ligand **3** plane (Figure 7, a). In the crystal lattice, the heteroduplex cations of **9** associate by ***off*** interactions between the lateral pyridine moieties of ligand **3** (average π-π stacking centroid–centroid distances of 3.80 Å), forming parallel layers (Figure 7, b). In the other direction, each layer is alternatively stratified above another by stacking of the terminal phenyl moieties of the ligand **2**, such that each layer is in van der Waals contact (average distance of 4.05 Å).

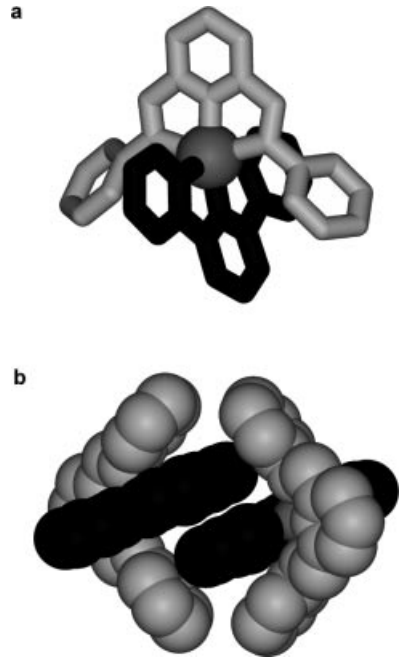


Figure 6. Crystal structure of the heteroduplex complex **8**: a) side view in stick representation (the Zn^{2+} ion is shown as a gray sphere); b) space-filling representation of the crystal packing.

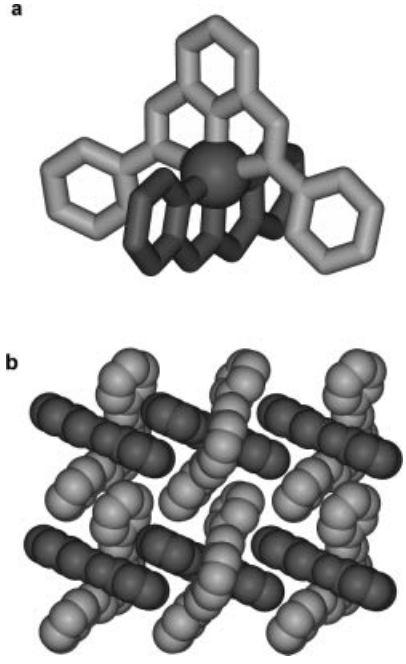


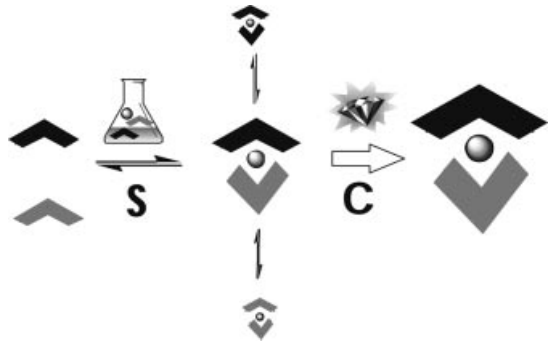
Figure 7. Crystal structure of the heteroduplex complex **9**: a) side view in stick representation (the Zn^{2+} ion is shown as a gray sphere); b) space-filling representation of the crystal packing.

The X-ray crystallographic results allow the following conclusions to be made. In term of specific self-assembly, the homo- and heteroduplex Zn^{2+} complexes of the terpyri-

dine-type ligands **1**–**3** self-organize in the solid state into 1D or 2D stacked layers (**4**, **7**, **9**), double-helix (**5**), or dimeric (**8**) architectures as a function of synergetic intra- and intermolecular π-π stacking interactions between different constitutional ligands. In terms of specific self-organization, the heteroduplex architectures **7**–**9** represent an attractive example of solid-state structures resulting from the synergistic effects of statistical (**7**, **9**) and structural-driven (**8**) binding of two different ligands by the Zn^{2+} metal ions.

Conclusions

This paper present the solid-state structures of homo- and heterocomplexes resulting from terpyridine-type ligands **1**–**3** and Zn^{2+} metal ions. The heteroduplex Zn^{2+} complexes **7**–**9** are quantitatively crystallized in the solid state by statistical (**7**, **9**) and structural (**8**) driven selection in solution from a binary mixture of the terpyridine-type complexes and are then trapped by crystallization in the solid state (Scheme 2).



Scheme 2. Statistical pre-amplification in solution (**S**) and solid-state selection process (**C**) of the heteroduplex complexes **7**–**9**.

The crystal structures and their packing present common features with many other similar architectures reported up to now.[5] However, their structural concept − octahedral Zn^{2+} coordination, positioning two ligands in an orthogonal position such that they further interact by π-π stacking in the crystal − allows us to obtain different 1D or 2D stacked layers (**4**, **7**, **9**), double-helix (**5**), or dimeric (**8**) architectures.

A further step toward such nanosystems 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

General Methods: 2,6-Pyridinedicarboxaldehyde, 2,2′:6′,2′′-terpyridine (**1**), 2-pyridinecarboxaldehyde, and 2-pyridylhydrazine 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 over sodium sulfate (Na_2SO_4).

^{1}H NMR, COSY, and ROESY spectra were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$ and CD_3CN, 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 2+). Samples were dissolved in acetonitrile and were continuously introduced into the mass spectrometer at a flow rate of 10 mL min^{-1} with a Waters 616HPLC pump. The temperature (60 °C) and the extraction cone voltage (5–10 V) were usually set to avoid fragmentations. The numerotations used for the assignments of the ^{1}H NMR signals (according to the corresponding COSY and ROESY spectra) are given below.

Synthesis of Ligands and Complexes: The pyridine-based ligands **2**[6] and **3**[7] were prepared according to the procedures described in the literature. Their NMR, ESI-mass spectra, and elemental analyses are consistent with analytically pure compounds.

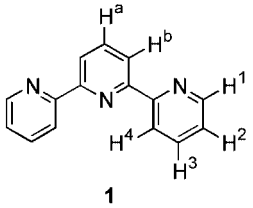
General Procedure for the Preparation of Zn^{II} Homoduplex Complexes 4–6: The reactions were performed typically on a 10-mg scale of ligand. The ligands **1–3** (0.035 mmol) and $Zn(CF_3SO_3)_2$ (0.0175 mmol) were dissolved in CD_3CN (1 mL), and stirred overnight at 60 °C.

$[Zn(1)_2](CF_3SO_3)_2$ (4): ^{1}HNMR (300 MHz, CD_3CN): δ = 8.81–8.78 (d, ^1J = 6.6 Hz, 4 H, H^b), 8.75–8.73 (t, ^2J = 6.6 Hz, 2 H, H^a), 8.60–8.57 (d, ^1J = 7.91 Hz, 4 H, H^4), 8.19-8.13 (td, ^2J = 7.91 Hz, 4 H, H^3), 7.78–7.76 (d, ^1J = 4.71 Hz, 4 H, H^1), 7.42–7.37 (td, ^2J = 5.28 Hz, 4 H, H^2) ppm. MS (ESI): *m*/*z* (%) = 265.5 (100) $[Zn(\mathbf{1})_2]^{2+}$.

$[Zn(2)_2](CF_3SO_3)_2$ (5): ^{1}HNMR (300 MHz, CD_3CN): δ = 8.81 (s, 4 H, H^1), 8.61–8.55 (t, ^2J = 8.1, J = 7.5 Hz, 2 H, H^a), 8.27–8.24 (d, ^1J = 7.8 Hz, 4 H, H^b), 7.36–7.26 (m, 12 H, H^{3+4}), 6.82–6.79 (d, ^1J = 3.6 Hz, 8 H, H^2) ppm. MS (ESI): *m*/*z* (%) = 317.7 (100) $[Zn(\mathbf{3})_2]^{2+}$.

$[Zn(3)_2](CF_3SO_3)_2$ (6): ^{1}HNMR (300 MHz, CD_3CN): δ = 8.61 (s, 2 H, H^5), 8.19–8.17 (d, ^1J = 4.52 Hz, 2 H, H^1), 8.12–8.07 (t, ^2J = 7.72 Hz, 2 H, H^3), 7.92-7.86 (m, 4 H, H^{8+4}), 7.80–7.78 (d, ^1J = 4.71 Hz, 2 H, H^{10}), 7.49–7.44 (td, ^2J = 5.27 Hz, 2 H, H^2), 7.21-7.19 (d, ^1J = 8.48 Hz, 2 H, H^7), 6.99–6.95 (td, ^1J = 4.53 Hz, 2 H, H^9) ppm. MS (ESI): *m*/*z* (%) = 230.4 (25) $[Zn(\mathbf{3})_2]^{2+}$, 251.0 (100) $[Zn(\mathbf{3})_2 + CH_3CN]^{2+}$, 259.9 (10) $[Zn(\mathbf{3})_2 + CH_3CN + H_2O]^{2+}$, 271.6 (75) $[Zn(\mathbf{3})_2 + 2\ CH_3CN]^{2+}$, 280.4 (20) $[Zn(\mathbf{3})_2 + 2\ CH_3CN + 2\ H_2O]^{2+}$.

General Procedure for the Preparation of Zn^{II} Homo and Heteroduplex Complex Combinatorial Libraries: Stoichiometric binary solu-



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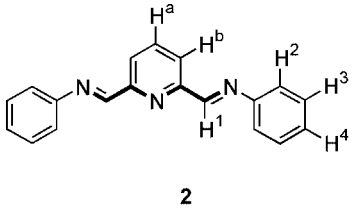

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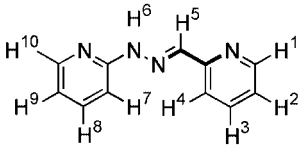

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Table 1. Crystallographic data for complexes **4**, **5**, **7**, **8**, and **9**.

	4	**5**	**7**	**8**	**9**
Formula	$C_{32}H_{22}F_6N_6O_6S_2Zn$	$C_{44}H_{36}F_6N_8O_6S_2Zn$	$C_{65}H_{49}F_{12}N_{14}O_{12}S_4Zn_2$	$C_{38}H_{29}F_6N_7O_6S_2Zn$	$C_{34}H_{27}F_6N_8O_6S_2Zn$
M_r	830	1016	1705	923	887
Space group	*Pnca*	$P22_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	9.0838(3)	8.2081(3)	13.8360(10)	10.9922(7)	10.1927(8)
b [Å]	16.8483(7)	14.5003(5)	14.022(2)	25.3050(10)	20.5260(10)
c [Å]	21.2904(7)	18.7227(7)	21.774(2)	14.3410(9)	17.6730(10)
α [°]	90	90	80.985(9)	90	90
β [°]	90	90	83.609(9)	93.642(5)	91.976(6)
γ [°]	90	90	61.970(10)	90	90
V [Å^3]	3258.4(2)	2228.37(14)	3679.3(8)	3981.0(4)	3695.3(4)
Z	4	2	2	4	4
Crystal size [mm]	0.20×0.22×0.24	0.17×0.25×0.38	0.08×0.26×0.40	0.11×0.13×0.50	0.08×0.10×0.32
Solvent	acetonitrile/ diisopropyl ether	acetonitrile/ diisopropyl ether	acetonitrile/ benzene	acetonitrile/ diisopropyl ether	acetonitrile/ diisopropyl ether
ρ [g cm^{-3}]	1.692	1.520	1.539	1.540	1.595
θ_{max} [°]	32.39	32.38	32.35	32.35	32.39
N_{ref}(tot)	63659	42552	67244	75361	70056
N_{ref} unique [$I > 2\sigma(I)$]	1884	5195	3432	2368	1843
N_{par}	242	304	380	246	229
R_1	0.0244	0.0362	0.1155	0.0676	0.0570
wR_2	0.0405	0.0387	0.1838	0.0950	0.0603

tions (1:1, molar ratio) of homoduplex complexes **4**–**6** in CD_3CN were mixed and stirred overnight at 60 °C. Stoichiometric binary solutions (1:1, molar ratio) of binary mixtures of ligands **1**–**3** in CD_3CN were mixed with the stoichiometric amount of metal ions and stirred overnight at 60 °C. These solutions were monitored by ^{1}H NMR spectroscopy and ESI mass spectrometry.

X-ray Crystallographic Data for Complexes 4, 5, 7, 8, and 9: All X-ray diffraction data were collected on an Xcalibur-I diffractometer (Oxford Diffraction) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at the joint X-ray scattering service of the Institut Européen des Membranes and the Institut Charles Gerhardt of the Université de Montpellier II. All measurements were carried out at 173 K using ω-scans after having placed the crystals in oil. All structures were solved using SIR2002;[15a] refinements were carried out using CRYSTALS[15b] 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 ratio did not allow us to do this. Details of the refinements and data collections can be found in Table 1.

CCDC-266698–266702 (for **4**, **5**, **7**, **8**, and **9**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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