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Self-sorting of Dynamic Metallosupramolecular Libraries DMLs via Metal-Driven Selection

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“Metal-driven” selection between finite mononuclear and polymeric metallosupramolecular species can be quantitatively achieved in solution and in crystalline state via coupled coordination/stacking interactional algorithms within Dynamic Metallosupramolecular Libraries- DMLs.

Self-organization of metallosupramolecular architectures is based on the implementation of ligands and of metal ions mutually reading out the structural information through the interactional algorithms.¹ Multiple constitutional interactions^{2,3} shed light on strategies used to dynamically drive the coordination (molecular) and the self-assembly (supramolecular) processes under the pressure of interactional algorithms (i.e. stacking, H-bond, etc.), toward complex systems: double helices,⁴ grids,⁵ borromean rings,⁶ capsules⁷, polygons,⁸ zippers,⁹ etc. We have recently demonstrated that simple/double level Dynamic Metallosupramolecular Libraries- DMLs can be generated via ligand and ligand/imine reversible exchanges. The metal ion coordination is positioning the ligands in close proximity. It results that reversible molecular imine exchanges and supramolecular non-covalent interactions may synergetically occur within a restricted interactional space, defined by the coordination geometry around the metal centers.¹⁰⁻¹² A rather unconventional and so far partially uncharted option for information storage is the multiple coding, offered by ligands in the process of simultaneous coordination with mixtures of metal cations, producing DMLs of mononuclear and polynuclear components containing distinct metal ions.^{5c}

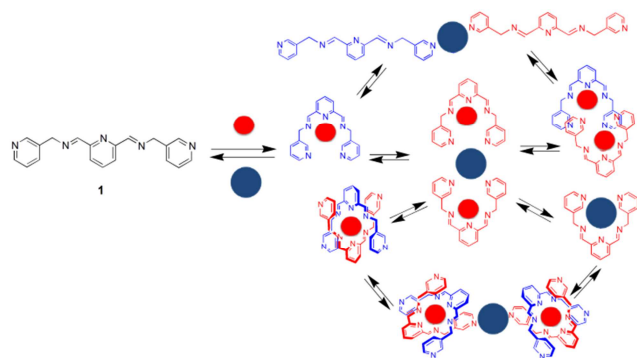


Figure 1. Dynamic Metallosupramolecular Library generated on simultaneous addition of two metal ions to ligand **1** which could be selectively expressed as an independent (linear) or interfering (cross-over) combination of the above coordination events.

It is reminiscent to a morphologically dynamic polyimine system can be switched between two macrocyclic and polymeric constitutional states via metal ion-coordination.¹³

Such competitive constitutional equilibria may be generated by employing ligand **1** and mixtures of metal ions in order to generate all possible interconverting combinations and geometries. It might allow the self-selection of a metal-ion specific constituent from an equilibrating collection of finite mononuclear and polymeric metallosupramolecular species (Fig. 1). The ligand **1** under conditions in which available pseudo-terpyridine (terpy) and pyridine side-arm (py) coordination sites can be involved respectively in the octahedral and linear coordination binding events of the metal ions, depending on experimental condition such as: metal ion nature, concentration, ligand: metal molar ratio, etc (Fig. 1).

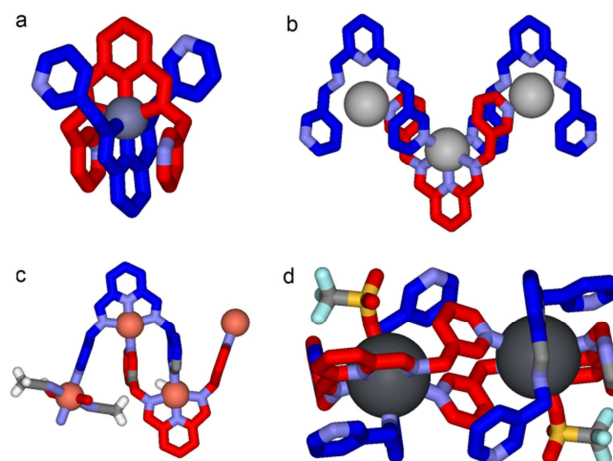


Figure 2. Crystal structure (stick representation) of the ligand **1**-complexes a) 1_2Zn^{2+} , b) 1Ag^+ , c) 1Cu^{2+} and d) 1_2Pb^{2+} . The metal ions are shown as blue (Zn^{2+}), light grey (Ag^+) red-brown (Cu^{2+}) and grey Pb^{2+} spheres. The non-coordinating TF^- anions and the H-atoms have been omitted for clarity.

This is revealed by the structurally different architectures obtained with different metal ions (Fig. 2, see a detailed description of the X-ray structures in ESI):

a) In the crystal of the Zn^{2+} complex, two ligands **1** are strongly intertwined stabilizing a duplex superstructure, 1_2Zn^{2+} (Fig. 2a). The relative position of the duplex ligands allows an internal overlap between the pyridyl moieties and the central pyridine moiety. Attempts to crystallize the monoligand complex 1Zn^{2+} failed, as previously observed for similar ligands,^{11b} proving the high stability of the duplex

structure $\mathbf{1}_2\text{Zn}^{2+}$. Only monocrystals of the duplex, $\mathbf{1}_2\text{Zn}^{2+}$ with no formation of any other solid phase can be obtained from stoichiometric binary mixtures ($\mathbf{1}:\text{Zn}^{2+} 1:>1$, mol:mol).

b) In the crystal of Ag^+ (Fig. 2b) and Cu^{2+} (Fig. 2c) complexes the two ligands $\mathbf{1}$ and two metal ions form the dimeric self-complementary molecular clefts,^{9a,b} each $[\mathbf{1}\text{Ag}^+]$ or $[\mathbf{1}\text{Cu}^{2+}]$ entity being slotted into the other. The Ag^+ and Cu^{2+} cations are coordinated by one terpy unit of the ligand \mathbf{a} and by the two (Ag^+) and respectively one (Cu^{2+}) pyridine side-arm(s) of vicinal ligands \mathbf{a}' . While the Ag^+ metal ions preserve the rare pentacoordinated geometry, resulting in the formation of a polymeric complex, the Cu^{2+} ions exist in two different geometries: the inner two cleft-structuring Cu^{2+} ions possess pentacoordinating donor sets $\text{Cu}^{2+}(\text{Terpy}:\text{Py}:\text{H}_2\text{O})$ and the outer two Cu^{2+} are ligated by the second pyridine side arm, two AcCN and two H_2O molecules.

c) The X-ray structural analysis of $\mathbf{1}_2\text{Pb}^{2+}$ crystals revealed the octacoordinated $\text{Pb}^{2+}(\text{Terpy}_2:\text{Py}:\text{CF}_3\text{SO}_3)$ cations, by two ligands of $\mathbf{1}$, resulting in the formation of the duplex superstructure, $\mathbf{1}_2\text{Pb}^{2+}$ (Fig. 2d). In the crystal, we observe the formation of dimers between $\mathbf{1}_2\text{Pb}^{2+}$ duplexes, each mononuclear complex being closely packed with the neighboring one via coordination of the Pb^{2+} to one pyridine arm of vicinal ligands.

The X-ray crystallographic results allow the following conclusions to be made :

1) In term of constitutional diversity the mononuclear, $\mathbf{1}_2\text{Zn}^{2+}$, dinuclear $[\mathbf{1}_2\text{Pb}^{2+}]_2$ $[\mathbf{1}\text{Ag}^+]_n$ and polymeric $[\mathbf{1}\text{Cu}^{2+}]_2$ metallosupramolecular architectures represent attractive arrays accessible in a single operational step by the combination of distinct metal-coordination behaviours and stabilized by π - π stacking interactions.

2) The ligand $\mathbf{1}$ is an excellent candidate for the generation of DMLs over a wide range of ligand:metal ion ratios and mixtures, resulting in the virtual formation of interexchanging equilibrating mixture of low-nuclear and polymeric species, from which the most stable constitutional states can be selected in solution and in the solid state by specific coordination/morphological information algorithms *via* the kinetically irreversible processes.¹⁰⁻¹²

Within this context, mixtures of $\mathbf{1}:\text{Zn}^{2+}$ and $\mathbf{1}:\text{Ag}^+$ in 2:1 and 1:1 ratios (mol:mol) in CD_3CN , result in the formation of inter-exchanging species in solution: $\mathbf{1}_2\text{Zn}^{2+} / \mathbf{1}_2\text{Ag}^+ / [\mathbf{1}\text{Ag}^+]_n$ and $\mathbf{1}_2\text{Zn}^{2+} / \mathbf{1}\text{Zn}^{2+} / [\mathbf{1}\text{Ag}^+]_n$, respectively, as proved by the $^1\text{H-NMR}$ (Fig. 3) and ESI-MS spectra (ESI). In all the cases, the reaction take place within 1 min. and the resulting mixtures would not change even when left for prolonged time to react or if heated. Crystals of $\mathbf{1}_2\text{Zn}^{2+}$ and $[\mathbf{1}\text{Ag}^+]_n$ suitable for X-ray analysis were formed also within minutes from CD_3CN solutions of $\mathbf{1}:\text{Zn}^{2+} 2:1$ and $\mathbf{1}:\text{Ag}^+ 1:1$ mixtures, respectively. Things became interesting when the $\mathbf{1}_2\text{Zn}^{2+}$ and $[\mathbf{1}\text{Ag}^+]_n$ complexes are the unique crystallizing compounds from the reaction mixtures of $\mathbf{1}:\text{Zn}^{2+} 1:1$ and $\mathbf{1}:\text{Ag}^+ 2:1$, stoichiometries, containing the products $\mathbf{1}\text{Zn}^{2+}$ and $\mathbf{1}_2\text{Ag}^+$ in solution, as proved by ESI-MS spectrometry. The crystals $[\mathbf{1}\text{Ag}^+]_n$ that formed under sub-stoichiometry when adding 0.5 eq. of Ag^+ prove that octahedral coordination of silver is enthalpically disfaored to the pentacoordinated one, probably

more stabilized via π - π stacking interactions between central pyridine of $\mathbf{1}$ and pyridine pendant arms. Then, we evaluated the selectivity of the ligand $\mathbf{1}$ towards a mixture of $\text{Zn}^{2+} / \text{Ag}^+ / \text{Pb}^{2+}$ metal ions at different stoichiometries:

a) Interestingly enough, the NMR spectra of the solutions of $\mathbf{1}:\text{Zn}^{2+}:\text{Ag}^+$ and $\mathbf{1}:\text{Zn}^{2+}:\text{Pb}^{2+} 2:1 :1$, mol : mol : mol, show exclusive formation after 3 minutes of the $\mathbf{1}_2\text{Zn}^{2+}$ complex with no traces of the $\mathbf{1}_2\text{Ag}^+$ (Fig. 3a) and $[\mathbf{1}_2\text{Pb}^{2+}]_2$ complexes, which further crystalized as $\mathbf{1}_2\text{Zn}^{2+}$ (see condition in SI). Moreover if 1 mol of Zn^{2+} is added to the precipitated formed in a $\mathbf{1}:\text{Ag}^+:\text{Pb}^{2+} 2:1 :1$, mol : mol : mol CD_3CN solution (probably a mixture of metallosupramolecular polymers), the precipitate is completely dissolving with the formation of $\mathbf{1}_2\text{Zn}^{2+}$ complex.

b) For the case of a solution $\mathbf{1}:\text{Zn}^{2+}:\text{Ag}^+$, 1: 1: 1, the reaction took place in a different manner. After 3 min. the NMR spectra revealed the formation of $\mathbf{1}_2\text{Zn}^{2+}$ and an unknown complex which gives signals that can not be recognized in any other complex spectrum, suggesting the formation of a hybrid complex wich contains both metals in its structure. After the reaction equilibrated itself in 60 minutes, the predominant compound in solution was $\mathbf{1}\text{Zn}^{2+}$. Crystallization did not occur from this mixture, again suggesting the interference of the silver cation in the process of the crystal matrix formation.

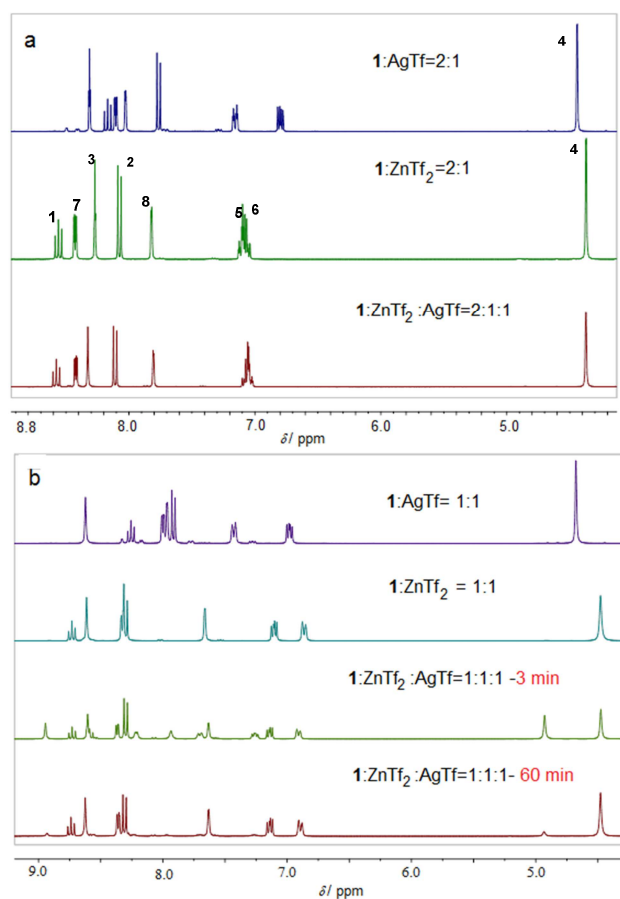


Figure 3. (a) $^1\text{H-NMR}$ spectra section in CD_3CN of the solutions (from top to bottom) of $\mathbf{1}:\text{Ag}^+ 2:1$, mol:mol; $\mathbf{1}:\text{Zn}^{2+} 2:1$ mol:mol and $\mathbf{1}:\text{Zn}^{2+}:\text{Ag}^+ 2:1:1$ mol:mol:mol; . (b) $^1\text{H-NMR}$ spectra section in CD_3CN of the solutions (from top to bottom) of $\mathbf{1}:\text{Ag}^+ 1:1$, mol:mol; $\mathbf{1}:\text{Zn}^{2+} 1:1$ mol:mol and $\mathbf{1}:\text{Zn}^{2+}:\text{Ag}^+ 1:1:1$ mol:mol:mol, after 3 and 60 min, respectively.

The preferential amplification of 1_2Zn^{2+} and of $1_2\text{Zn}^{2+} / 1\text{Zn}^{2+}$ and further crystallization of 1_2Zn^{2+} from a solution of ligand **1** and a mixture of Zn^{2+} and Ag^+ and Pb^{2+} metal ions confirms our previous observations of the formation of the entropically-
5 favored highly packed mononuclear architectures compared to the multinuclear, dimeric $[\text{1}_2\text{Pb}^{2+}]_2$ or polymeric $[\text{1Ag}^+]_n$ ones. The entropic cost of binding to metal ion to the free ligands must be far larger for the polymeric systems than the case where these ligands are bound in compact and robust
10 monoclusters with restricted conformational entropy.

Finally, we have been interested to evaluate the competitive selection/amplification of $\text{Zn}^{2+} / \text{Ag}^+$ metal ions towards different ligands. For this reason, we decided to use benzylamine as a competitor for the formation of the ligand.

15 A small ligand library has been obtained by mixing 1 eq. of dialdehyde and 0.5 equivalents each of 3-picolyl amine and benzylamine (Scheme 1S). We observed the statistical formation of a mixture ligands **1:3:2**. in 1:2:1 mol:mol:mol ratio, as previously observed.¹⁰ The addition of 0.5 eq. of Zn^{2+}
20 or 1.0 eq. of Ag^+ results in the formation of a complex mixture of six Zn^{2+} or Ag^+ complexes of all three ligands **1-3**, as previously demonstrated.^{10d} Interestingly again, through crystallization both of the solutions formed quantitatively
25 crystals of the single homocomplexes 1_2Zn^{2+} and $[\text{1Ag}^+]_n$, with the complete exclusion of ligands **2,3**.

The robustness of 1_2Zn^{2+} and $[\text{1Ag}^+]_n$ compounds results from compatibility and synergistic effect of the metal ion-binding and of the stacking interactions which are much stronger for the picolyl coordinative side-arms when
30 compared with the competitive benzyl ones.

In conclusion, the studies presented here reveals that the generation of DMLs over a range of ligand-metal structures and ratios, results in the formation of inter-exchanging equilibrating mixture of mononuclear, dinuclear or polymeric
35 species which converts into unique compact packed mononuclear compact species in solution and in the solid state via crystallization.^{11, 12} At this point, we want first to highlight the possible quantitative “metal-driven” selection in solution via coupled coordination/stacking interactional algorithms.
40 These mechanisms are robust enough to induce “ligand selection” from a dynamic pool of different ligands, **1-3**. It is based on the relative constitutional stability of crystalline duplex 1_2Zn^{2+} and or polymeric $[\text{1Ag}^+]_n$ cleft complexes, amplified from the complex mixtures in solution via a
45 kinetically-driven crystallization process.

A further step toward processes of increasing complexity could involve the ligands of different dimensionality or the library diversification by ligands undergoing structural reversible interconnections by chemical exchange.

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Notes and references

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