Electronic Supporting Information for

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

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**General methods:** All reagents were obtained from commercial suppliers and used without further purification. $^1$H NMR, were recorded on an ARX 300 MHz Bruker spectrometer in CD$_3$CN 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 through a Waters 616HPLC pump. The temperature (60°C), the extraction cone voltage ($V_c$=5-10V) was usually set to avoid fragmentations.

**Synthesis of ligands 1 and 2:** A mixture of 2,6 diformylpyridine (13,4 mg, 0.1 mmol) and 3-pycolil amine (21,6 mg, 0.2 mmol) and benzylamine (21,4, 0.2 mmol) respectively in CD$_3$CN, was stirred for 5 minutes at room temperature to produce quantitatively pure product 1 and 2 as shown by NMR analysis.$^{15,28}$

**Synthesis of the $^{1}_2$Zn$^{2+}$, [1Ag$^+$]$_n$ [1Cu$^{2+}$]$_2$ and $^{1}_2$Pb$^{2+}$]$_2$ complexes:** The reactions were performed typically on a 31,5 mg (0,1 mmol) scale of ligand. The ligands 1 or 2 and the corresponding metal triflate, Zn(CF$_3$SO$_3$)$_2$ (2:1 and 1:1, 1:Zn$^{2+}$ respectively 2:Zn$^{2+}$ mol:mol), Ag(CF$_3$SO$_3$) (2:1 and 1:1, 1:Ag$^+$ respectively 2:Ag$^+$ mol:mol), Pb(CF$_3$SO$_3$)$_2$ (1:1, 1:Pb$^{2+}$ mol:mol), Cu(CF$_3$SO$_3$)$_2$ (1:1, 1:Cu$^{2+}$ mol:mol) were dissolved in CD$_3$CN (1 mL) and stirred at room temperature for 1h. These solutions were monitored by $^1$H NMR and ESI mass spectrometry. Layering such solutions metal ion complexes in acetonitrile with the $i$-propylether in 1:4 volume ratio at room temperature, resulted in a unique set of single-crystals suitable for X-ray experiments.
Ligand 1: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.62 (d, 2H, $^4J$=1.8 Hz, H$_8$), 8.55 (t, 2H, $^4J$=1.2 Hz, H$_3$), 8.50 (dd, 2H, $^4J$=4.8 Hz, $^4J$=1.5 Hz, H$_7$), 8.07 (d, 2H, $^4J$=7.5 Hz, H$_2$), 7.89 (t, 2H, $^3J$=7.8 Hz H$_1$), 7.75 (dq, 2H, $^3J$=7.8 Hz, $^4J$=1.8 Hz H$_5$), 7.35 (m, 4H, H$_6$), 4.89 (s, 4H, H$_4$).

ES-MS: m/z (%): 316.0 (100) [M+1]$^+$

Ligand 2: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.52 (s, 2H, H$_3$), 8.05 (d, 2H, $^3J$=7.8 Hz, H$_2$), 7.87 (t, 1H, $^3J$=7.8 Hz, H$_1$), 7.35 (overlapped, 10H, H$_5$ + H$_6$ + H$_7$), 4.87 (s, 4H, H$_4$) ES-MS: m/z (%): 314.1 (100) [M+1]$^+$

Complex 1:Zn$^{2+}$: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.73 (t, 1H, $^3J$=7.8 Hz, H$_1$), 8.61 (s, 2H, H$_3$), 8.31 (m, 4H, H$_2$ + H$_7$), 7.66 (d, 2H, $^4J$=1.2 Hz, H$_8$), 7.10 (m, 2H, H$_6$), 6.86 (d, 2H, $^3J$=8.1 Hz, H$_5$), 4.48 (s, 4H, H$_4$). ES-MS: m/z (%): 347.0 (100) 1$Zn^{2+}$, 677.9 (80) 1(Tf)$_2$Zn.

Complex 1:Zn$^{2+}$: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.56 (t, 2H, $^3J$=7.8 Hz, H$_1$), 8.33 (dd, 4H, $^3J$=4.5 Hz, $^4J$=1.8 Hz, H$_7$), 8.27 (t, 4H, $^4J$=1.5 Hz, H$_3$), 8.07 (d, 4H, $^3J$=7.8 Hz, H$_2$), 7.82 (d, 4H, $^4J$=1.5 Hz, H$_8$), 7.09 (m, 8H, H$_5$ + H$_6$), 4.37 (d, 8H, $^4J$=1.2 Hz, H$_4$). ES-MS: m/z (%): 347.0 (100) 1$Zn^{2+}$, 843.1 (95) 1$Zn^{2+}$, 677.8 (40) 1(Tf)$_2$Zn.

Complex 2:Zn$^{2+}$: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.49 (t, 2H, $^3J$=7.8 Hz, H$_1$), 8.11 (t, 4H, $^4J$=1.2 Hz, H$_3$), 7.97 (d, 4H, $^3J$=7.8 Hz, H$_2$), 7.23 (tt, 4H, $^3J$=7.8 Hz, $^4J$=1.2 Hz, H$_7$), 7.02 (t, 8H, $^3J$=7.8 Hz, H$_6$), 6.59 (dd, 8H, $^3J$=7.8 Hz, $^4J$=1.2 Hz H$_5$), 4.37 (d, 8H, $^4J$=1.2 Hz, H$_4$).

ES-MS: m/z (%): 344.5 (100) 1$Zn^{2+}$, 840.1 (70) 1(Tf)$_2$Zn$^+$.

Complex [1Ag$^+$_]$_n$: $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ ppm 8.62 (s, 2H, H$_3$), 8.26 (t, 1H, $^3J$=7.8 Hz, H$_1$), 8.00 (dd, 2H, $^3J$=5.1 Hz, $^4J$=1.5 Hz, H$_7$), 7.96 (d, 2H, $^4J$=1.2 Hz, H$_8$), 7.91 (d, 2H
\[ ^3 \text{J}=7.8 \text{ Hz, H}_2, \] 7.42 (d, 2H, \[ ^3 \text{J}=7.8 \text{ Hz H}_3 \]), 6.98 (m, 2H, H_6), 4.67 (d, 2H, \[ ^3 \text{J}=7.8 \text{ Hz H}_7 \]).

ES-MS: m/z (%): 422.0 (100) \( \text{1Ag}^+ \), 424.0 (95) \( \text{1Ag}^+ \).

**Complex 1\(_2\)Ag\(^+\):** \(^1\text{H} \) NMR (300 MHz, CD\(_3\)CN): \( \delta \) ppm 8.31 (s, 4H, \( ^4\text{J}=1.8 \text{ Hz H}_3 \)), 8.17 (t, 2H \( ^3\text{J}=7.8 \text{ Hz, H}_1 \)), 8.11 (dd, 4H \( ^3\text{J}=4.8 \text{ Hz, } ^4\text{J}=1.8 \text{ Hz, H}_7 \)), 8.03 (d, 4H \( ^4\text{J}=1.8 \text{ Hz, H}_8 \)), 7.76 (d, 4H \( ^3\text{J}=7.8 \text{ Hz, H}_2 \)), 7.15 (dt, 4H, \( ^3\text{J}=8.1 \text{ Hz, } ^4\text{J}=1.8 \text{ Hz, H}_5 \)), 6.80 (m, 4H, H_6), 4.44 (d, 8H, \( ^4\text{J}=1.2 \text{ Hz H}_4 \)) ES-MS: m/z (%): 737.1 (100) \( \text{1}_2\text{Ag}^+ \), 739.1 (95) \( \text{1}_2\text{Ag}^+ \).

**Complex 2\(_2\)Ag\(^+\):** \(^1\text{H} \) NMR (300 MHz, CD\(_3\)CN): \( \delta \) ppm 8.45 (t, 2H, \( ^4\text{J}=1.5 \text{ Hz H}_3 \)), 8.25 (t, \( ^3\text{J}=7.8 \text{ Hz, H}_1 \)), 7.89 (d, 4H \( ^3\text{J}=7.8 \text{ Hz, H}_2 \)), 7.02 (overlapped, 10H, H_5 + H_6 + H_7 + H_8), 4.56 (d, 4H, \( ^4\text{J}=1.5 \text{ Hz H}_4 \)) ES-MS: m/z (%): 420.0 (100) \( \text{2Ag}^+ \), 422.0 (95) \( \text{2Ag}^+ \).

**Complex \([\text{1}_2\text{Pb}^{2+}]_2\):** NMR spectra shows indistinguishable broad peaks due to fast ligand exchange. ES-MS: m/z (%): 672 (70) \( \text{1}(\text{Tf})\text{Pb}^+ \).

**Complex \([\text{1}_2\text{Cu}^{2+}]_2\):** due to the paramagnetism of the copper cation no concludent NMR spectra could be recorded. ES-MS: m/z (%): 346.5 (100) \( \text{1}_2\text{Cu}^{2+} \), 842.1 (80) \( \text{1}_2(\text{Tf})\text{Cu}^+ \).

**X-ray Single Crystal Diffraction Data for complexes \([\text{1}_2\text{Zn}^{2+}]_2\), \([\text{1Ag}^+]_n \) [\( \text{1Cu}^{2+}]_2 \) and \([\text{1}_2\text{Pb}^{2+}]_2\):** All the structures have been measured on an Agilent Technologies Gemini-S four circle diffractometer using Mo-\( \text{K}\alpha \) radiation (\( \lambda = 0.71073 \text{ Å} \)) and equipped with a Sapphire3 detector at 175 K at the joint X-ray scattering facility of the Pôle Balard at the University of Montpellier, France. The structures have been solved using the \textit{ab-initio} charge flipping method as implemented in \textit{SUPERFLIP} (Palatinus & Chapuis, 2007). In the case of structures \([\text{1Ag}^+]_n \) and \([\text{1}_2\text{Pb}^{2+}]_2\) the disordered triflates were solved by refining two equivalent molecules at 0.5 occupancy. Hydrogen atom positions were determined using Fourier differential maps in the case of all the structures. All structures were initially refined using non-linear least-squares methods as implemented in \textit{CRYSTALS} (Betteridge et al, 2003), in which the hydrogen atoms were treated as riding on their parent atoms and with \( U_{iso}(H) \)
constrained to in general 1.2-1.5 times $U_{eq}(H)$ that of the parent atom. The final difference Fourier maps showed in many cases residual peaks due to bonding effects, because of the in general good resolution of the experimental data (0.8 Å for $[1 Ag^+]_n$, $[1 Cu^{2+}]_2$ and $[1 Pb^{2+}]_2$, 0.9 Å for $1 Zn^{2+}$, where the experimental resolution is defined according to Dauter (1999)).

Essential crystallographic information is gathered in Table 1S.

**Table 1S:** Crystallographic information on data collection and structure refinement for complexes $1 Zn^{2+}$, $[1 Ag^+]_n [1 Cu^{2+}]_2$ and $[1 Pb^{2+}]_2$

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<th>$1 Zn^{2+}$</th>
<th>$[1 Ag^+]_n$</th>
<th>$[1 Cu^{2+}]_2$</th>
<th>$[1 Pb^{2+}]_2$</th>
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<td>Formula</td>
<td>C$<em>{38}$H$</em>{34}$N$<em>{10}$Zn$</em>{0.5}$(CF$_3$SO$_3$)</td>
<td>C$<em>{50}$O$</em>{26}$SC$<em>{10}$H$</em>{17}$AgN$_5$,(CF$_3$SO$_3$)$_2$</td>
<td>C$<em>{56}$H$</em>{68}$N$_{20}$Pb$_2$(CF$_3$SO$_3$)$_4$</td>
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Crystal structure of $\text{1}_2\text{Zn}^{2+}$: In the crystal the two ligands are strongly intertwined in order to satisfy the octahedral coordination sphere of $\text{Zn}^{2+}$. In the duplex structure $\text{1}_2\text{Zn}^{2+}$ the $\text{Zn}^{2+}$ ions are fully coordinated by two ligands arranged into two nearly perpendicular (89.03°) planes and presents a distorted octahedral coordination geometry. The average $\text{Zn}^{2+}$-$\text{N}_{\text{Pyridine}}$ and $\text{Zn}^{2+}$-$\text{N}_{\text{imine}}$, distances are 2.051 and 2.244 Å, respectively. The relative position of the duplex ligands allows the pyridil moieties from two adjacent complexes to pi-stack, with an average centroid-centroid distances of 3.675 Å corresponding to a $\pi$-$\pi$ stacking contact. Attempts to crystallize the monoligand complex $\text{1Zn}^{2+}$: complex failed, proving the nice stability of duplex structures $\text{1}_2\text{Zn}^{2+}$ and only monocrystals of the duplex, with no formation of any other solid phase obtained from stoichiometric binary mixtures (1:1, mol:mol) of different solution-diffusion experiments. Although the crystallization yield was relatively high, the quality of the harvested crystals was low and complete data could be recorded only up to 0.9 Å resolution. Two triflate anions are are filling the interstices between the complexes so that all available space is filled and for charge balancing purposes(Figure 2S-4S). One of these triflates proved to be highly disordered.

Fig. 1S. Coordination sphere of $\text{Zn}^{2+}$ in $\text{1}_2\text{Zn}^{2+}$
Fig. 2S. Packing of [1[Zn^{2+}] along a

Fig. 3S. Packing of [1[Zn^{2+}] along b
Fig. 4S. Packing of 1$_2$Zn$^{2+}$ along $c$

**Crystal structure of [1Ag$^+$]$_n$:** In the [1Ag$^+$]$_n$ structures two ligands 1 and the Ag$^+$ metal ions form the dimeric self-complimentary molecular clefts, each [1M$^+$] entity being slotted into the other. The Ag$^+$ cations are coordinated by one terpy unit of the ligand a (the average Ag$^+$-N distances are 2.54 Å) and by the pyridine side arm of the ligand a’ (the average Ag$^+$-N is 2.264 Å, respectively). The Ag$^+$-N cations present a trigonal bipyramidal coordination geometry.
The formation of the self-complementary [1Ag⁺]ₙ molecular clefts does not impose any interactions between adjacent polymeric chains. The interstices are filled with triflate counterions.

Fig. 5S. Coordination sphere of Ag⁺ in [1Ag⁺]ₙ (uncoordinating residues have been omitted for clarity)
Fig. 6S. Packing of $[\text{Ag}^+]_n$ along $a$

Fig. 7S. Packing of $[\text{Ag}^+]_n$ along $b$
Fig. 8S. Packing of $[\text{Ag}^+]_n$ along $c$

**Crystal structure of $[\text{Cu}^{2+}]_2$:** Structure $[\text{Cu}^{2+}]_2$ has two distinct types of $\text{Cu}^{2+}$ ions. In both cases the copper cation presents an octahedral coordination sphere. Ligands 1 and $\text{Cu}^{2+}$ metal ions form the dimeric self-complimentary molecular clefts, each $[\text{1M}^+]$ entity being slotted into the other. The $\text{Cu}^{2+}$ cations are coordinated by one terpy unit of the ligand $a$ (the average $\text{Cu}^{2+}$-N distances are 2.036 Å) and by the pyridine side arm of the ligand $a'$ (Cu$^{2+}$-N distance is 1.974 Å). The octahedral coordination sphere is completed by a triflate oxygen with the Cu$^{2+}$-O distance of 3.001 Å. These clefts are tied together by Cu$^{2+}$ cations coordinated by two pyridine moieties (Cu$^{2+}$-N distance is 2.036 Å), two water (average Cu$^{2+}$-OH$_2$ distance is 2.015 Å) and two acetonitrile molecules (the average Cu$^{2+}$-NCAc distance is 2.385 Å). Charge balance is provided by triflate anions.
Fig. 9S. Coordination sphere of Cu$^+$ in [1Cu$^{2+}$]$_2$ (uncoordinating residues have been omitted for clarity)
Fig. 10S. Packing of [1Cu$^{2+}$]$_2$ along $a$

Fig. 11S. Packing of [1Cu$^{2+}$]$_2$ along $b$

Fig. 12S. Packing of [1Cu$^{2+}$]$_2$ along $c$
Crystal structure of $\text{I}_2\text{Pb}^{2+}$: The X-ray structural analysis of $\text{I}_2\text{Pb}^{2+}$ crystals reveals the Pb$^{2+}$ cations being coordinated by three ligands of 1, two forming a cleft (average $d_{\text{Pb}^{2+}}$-$\text{NPyridine}$ = 2.630 Å and $d_{\text{Pb}^{2+}}$-$\text{Nimine}$ = 2.755 Å) and pyridyl group from a third connecting adjacent complex ($d_{\text{Pb}^{2+}}$-$\text{NPyridine}$ = 2.847 Å), and one triflate anion ($d_{\text{Pb}^{2+}}$-$\text{OTrif}$ = 2.757 Å). It should be noted that while the $d_{\text{Pb}^{2+}}$-$\text{NPyridine}$ distance varies only by approximately 0.2 Å, the $d_{\text{Pb}^{2+}}$-$\text{Nimine}$ distances vary by about 0.4 Å. In the crystal the communication between $\text{I}_3\text{Pb}^{2+}$ duplexes is realized via the supplementary coordinative interaction by the pyridine side arm of the neighboring duplex, each mononuclear complex being closely packed with its neighbor, resulting in the formation of polymeric chains along the $a$ axis (Figures 14S-16S). With the exception of coordination bonds, no other strong interactions are observed, which would indicate that the main crystallization force is satisfying the large coordination sphere of Pb$^{2+}$. Triflate counterions provide charge balance and fill the interstices. The uncoordinated triflate is significantly disordered.

Fig. 13S. Coordination sphere of Pb$^{2+}$ in $\text{I}_2\text{Pb}^{2+}$ (uncoordinating residues have been omitted for clarity)
Fig. 14S. Packing of \( \text{Pb}^{2+} \) along \( a \)
Fig. 15S. Packing of $\text{I}_2\text{Pb}^{2+}$ along $b$
Fig. 16S. Packing of $\text{I}_2\text{Pb}^{2+}$ along $c$

**Crystal structure of $\text{I}_2\text{Zn}^{2+}$**: Crystal structure has been reported and described in previous paper.$^3$
Dynamic Metallosupramolecular Libraries- DMLs: We conducted a series of reactions using different mixtures of ligands and metals in various equivalents to be able to follow the complex formation in the library (Table 2S).

Experimental procedure: a) homoligand libraries: a small library has been obtained by mixing either ligand 1 or 2 with a mixture of 0.5 or 1 equivalents of Zn(CF$_3$SO$_3$)$_2$ and Ag(CF$_3$SO$_3$) in CD$_3$CN. The formation of the complexes has been monitored thorough NMR. By comparing the spectra obtained from the libraries with the spectra from each separate complex we could determine the formation of one or the other complex in each library.

b) heteroligand libraries: a small ligand library has been obtained by mixing 1 eq. of dialdehyde and 0.5 equivalents each of 3-pycolyl amine and benzylamine (Scheme 1S). To the obtained mixture of ligands 0.5 or 1 equivalents of Zn(CF$_3$SO$_3$)$_2$ and Ag(CF$_3$SO$_3$) has been added in CD$_3$CN.

![Scheme 1S.](image)

Figure 17S. $^1$H-NMR spectra section in CD$_3$CN of the library containing ligands 1, 2 and 3
Table 2S. Table representation of reactions specifying the compounds formed in solution and in solid state

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<tr>
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<td>Ag(L2)$_2$</td>
</tr>
<tr>
<td>14</td>
<td>AL R2</td>
<td>0.5 Eq Zn</td>
<td>0.5 Eq Ag</td>
</tr>
<tr>
<td>15</td>
<td>AL R2</td>
<td>1 Eq Zn</td>
<td>1 Eq Ag</td>
</tr>
<tr>
<td>16</td>
<td>AL R1</td>
<td>R2 0.5 Eq Zn</td>
<td>1 Eq Ag</td>
</tr>
<tr>
<td>17</td>
<td>AL R1</td>
<td>R2 1 Eq Ag</td>
<td>mix</td>
</tr>
</tbody>
</table>

Interpreting the results (Table 2S) we have drawn several conclusions regarding the selectivity of the ligands. Using mixtures of zinc and silver always produce complexes with selectivity towards the zinc. Using different equivalents of metals in some cases (2, 3, 13, 14) produce different products in solution from the ones formed through crystallization. When comparing the use of pycolilamine against benzylamine the lack of the nitrogen atom in the second case manifests itself when using different equivalents of Zn. In the case of ligand 1 at different equivalents two individual compounds form in solution, both being resolved to the same crystal and as for ligand 2 there is only one compound that is observed through NMR in both cases in solution. When both amines were present in solution the NMR presented a mixture of complexes being formed with both Zn and Ag but through crystallization both of the solutions formed crystals with preference to single complex (13, 14).
