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.[1S, 2S]

Synthesis of the 1_2Zn^{2+}, [1Ag$^+$]$_n$ [1Cu^{2+}]$_2$ and [1_2Pb^{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.
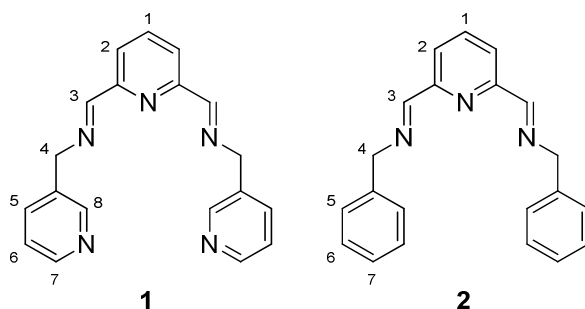
Ligand 1 : ^{1}H NMR (300 MHz, CD$_3$CN): δ ppm 8.62 (d, 2H ^3J=1,8 Hz, H$_8$), 8.55 (t, 2H, ^4J=1,2 Hz, H$_3$), 8.50 (dd, 2H ^3J=4,8 Hz, ^4J=1,5 Hz, H$_7$), 8.07 (d, 2H ^3J=7,5 Hz, H$_2$), 7.89 (t, 2H, ^3J=7,8 Hz H$_1$), 7.75 (dq, 2H ^3J=7,8 Hz, ^4J=1,8 Hz H$_5$), 7.35 (m, 4H, H$_6$),4.89 (s, 4H, H$_4$). ES-MS: m/z (%): 316.0 (100) [M+1]$^+$

Ligand 2 : ^{1}H NMR (300 MHz, CD$_3$CN): δ 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 1Zn^{2+}: ^{1}H NMR (300 MHz, CD$_3$CN): δ 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**$_2$Zn^{2+} , 677.9 (80) **1**(Tf)$_2$Zn.

Complex 1$_2$Zn^{2+} : ^{1}H NMR (300 MHz, CD$_3$CN): δ 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**$_2$Zn^{2+} , 843.1 (95) **1**$_2$(Tf)Zn$^+$,677.8 (40) **1**(Tf)$_2$Zn.

Complex 2$_2$Zn^{2+} : ^{1}H NMR (300 MHz, CD$_3$CN): δ 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**$_2$Zn^{2+} , 840.1 (70) **1**$_2$(Tf)Zn$^+$.

Complex [1Ag$^+$]$_n$, : ^{1}H NMR (300 MHz, CD$_3$CN): δ 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

^3J=7,8 Hz, H$_2$), 7,42 (d, 2H, ^3J=7,8 Hz H$_5$), 6,98 (m, 2H, H$_6$), 4,67 (d, 2H, ^3J=7,8 Hz H$_7$).

ES-MS: m/z (%): 422.0 (100) **1**Ag$^+$, 424.0 (95) **1**Ag$^+$.

Complex 1$_2$Ag$^+$: ^{1}H NMR (300 MHz, CD$_3$CN): δ ppm 8.31 (s, 4H, ^4J=1,8 Hz H$_3$), 8.17 (t,

2H ^3J=7,8 Hz, H$_1$), 8.11 (dd, 4H ^3J=4,8 Hz, ^4J=1,8 Hz, H$_7$), 8,03 (d, 4H ^4J=1,8 Hz, H$_8$), 7,76

(d, 4H ^3J=7,8 Hz, H$_2$), 7,15 (dt, 4H, ^3J=8,1 Hz, ^4J=1,8 Hz H$_5$), 6,80 (m, 4H, H$_6$), 4,44 (d, 8H,

^4J=1,2 Hz H$_4$) ES-MS: m/z (%): 737.1 (100) **1$_2$**Ag$^+$, 739.1 (95) **1$_2$**Ag$^+$

Complex 2Ag$^+$: ^{1}H NMR (300 MHz, CD$_3$CN): δ ppm 8.45 (t, 2H, ^4J=1,5 Hz H$_3$), 8.25 (t, 1H

^3J=7,8 Hz, H$_1$), 7.89 (d, 4H ^3J=7,8 Hz H$_2$), 7.02 (overlapped, 10H, H$_5$ + H$_6$ + H$_7$ + H$_8$), 4.56

(d, 4H, ^4J=1,5 Hz H$_4$). ES-MS: m/z (%): 420.0 (100) **2**Ag$^+$, 422.0 (95) **2**Ag$^+$.

Complex [1$_2$Pb^{2+}]$_2$: NMR spectra shows indistinguishable broad peaks due to fast ligand

exchange. ES-MS: m/z (%): 672 (70) **1**(Tf)Pb$^+$.

Complex 1$_2$Cu^{2+} : due to the paramagnetism of the copper cation no concludent NMR spectra

could be recorded. ES-MS: m/z (%): 346.5 (100) **1$_2$**Cu^{2+}, 842.1 (80) **1$_2$**(Tf)Cu$^+$.

**X-ray Single Crystal Diffraction Data for complexes 1$_2$Zn^{2+}, [1Ag$^+$]$_n$ [1Cu^{2+}]$_2$ and

[1$_2$Pb^{2+}]$_2$** : All the structures have been measured on an Agilent Technologies Gemini-S four

circle diffractometer using Mo-$K\alpha$ radiation (λ = 0.71073 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 *ab-initio* charge flipping

method as implemented in *SUPERFLIP* (Palatinus & Chapuis, 2007). In the case of structures

[1Ag$^+$]$_n$ and [1$_2$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 *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 $[1Ag^+]_n$, $[1Cu^{2+}]_2$ and $[1_2Pb^{2+}]_2$, 0.9 Å for 1_2Zn^{2+}, where the experimental resolution is defined according to Dauter (1999)). Essential crystallographic information is gathered in Table 1**S.**

Table 1S: Crystallographic information on data collection and structure refinement for complexes 1_2Zn^{2+}, $[1Ag^+]_n$ $[1Cu^{2+}]_2$ and $[1_2Pb^{2+}]_2$

	1_2Zn^{2+}	$[1Ag^+]_n$	$[1Cu^{2+}]_2$	$[1_2Pb^{2+}]_2$
Formula	$C_{38}H_{34}N_{10}Zn_{0.5}(CF_3SO_3)$	$CF_3O_3SC_{19}H_{17}AgN_5,(CF_3SO_3)$	$C_{76}H_{68}N_{20}Pb_2(CF_3SO_3)_4$	$C_{42}H_{48}Cu_3N_{12}O_4(CF_3SO_3)_6, (H_2O)_2$
Crystal Class	Triclinic	triclinic	Monoclinic	triclinic
Space Group	P-1	P-1	I2/c	P-1
a (Å)	10.8863(5)	9.2473(3)	23.4956(5)	12.4851(4)
b (Å)	11.9081(6)	10.7831(4)	11.8708(3)	12.9394(3)
c (Å)	17.5294(8)	12.8209(5)	31.4169(10)	13.0853(5)
α (°)	71.881(4)	94.960(3)	90	111.257(3)
β (°)	87.938(4)	107.524(3)	98.953(3)	105.181(3)
γ (°)	76.949(4)	110.985(3)	90	103.697(3)
Volume (Å^3)	2102.52(19)	1110.81(8)	8655.8(4)	1767.31(13)
Z	2	2	4	1
Radiation type	Mo-$K\alpha$	Mo-$K\alpha$	Mo-$K\alpha$	Mo-$K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
ρ (gcm^{-3})	1.570	1.711	1.743	1.791
Temperature (K)	175	175	175	175
Diffractometer type	Gemini-S	Gemini-S	Gemini-S	Gemini-S
Scan type	ω	ω	ω	ω
Reflections measured	14302	19879	25217	15005
Independent reflec.	5969	4818	8239	6523
Rint	0.027	0.031	0.034	0.030
Average size (mm)	0.300	0.300	0.200	0.300
Refinement on	F	F	F	F
R-factor	0.0430	0.0296	0.0331	0.0494
Weighted R-factor	0.0451	0.0368	0.0394	0.0494
σ(I) limit	2.000	2.000	2.000	2.000
Number of parameters	658	298	658	508
Goodness of fit	1.1870	1.0846	0.9956	0.9997

Crystal structure of 1_2Zn^{2+}: In the crystal the two ligands are strongly intertwined in order to satisfy the octahedral coordination sphere of Zn^{2+}. In the duplex structure 1_2Zn^{2+} the 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 Zn^{2+}-$N_{Pyridine}$ and Zn^{2+}-N_{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 π-π stacking contact. Attempts to crystallize the monoligand complex $1Zn^{2+}$: complex failed, proving the nice stability of duplex structures 1_2Zn^{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.
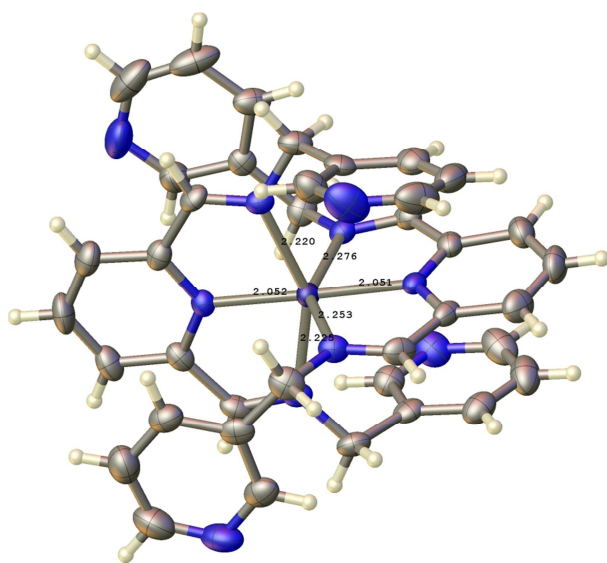
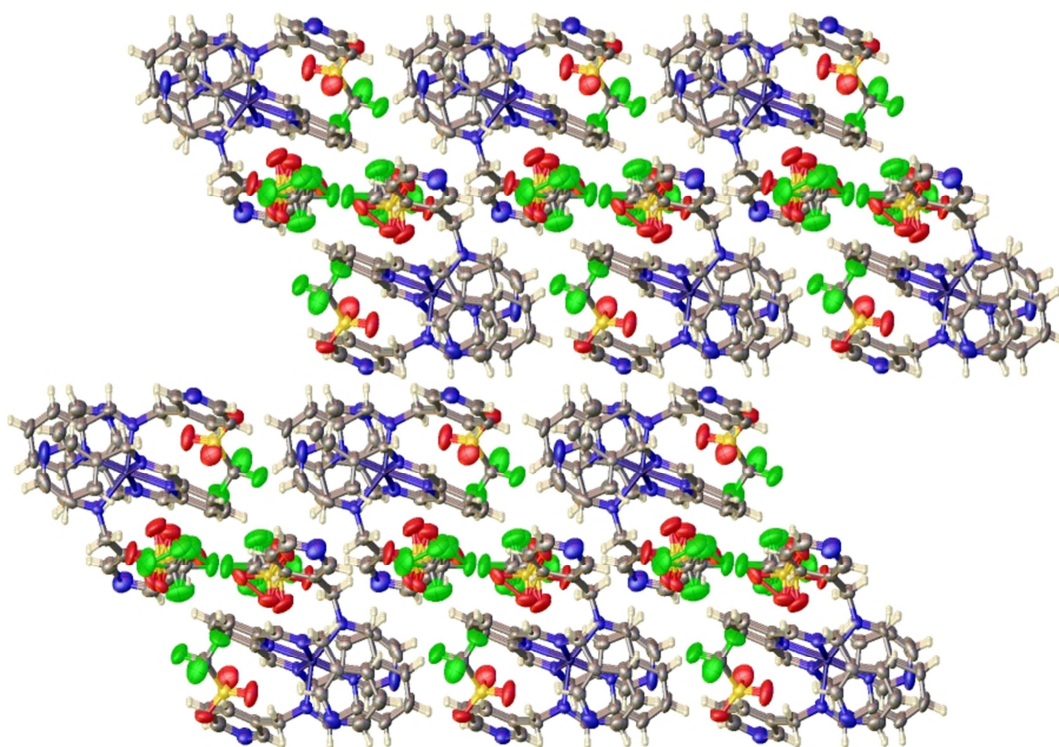Fig. 1S. Coordination sphere of Zn^{2+} in 1_2Zn^{2+}

Fig. 2S. Packing of $\mathbf{1}_2Zn^{2+}$ along a
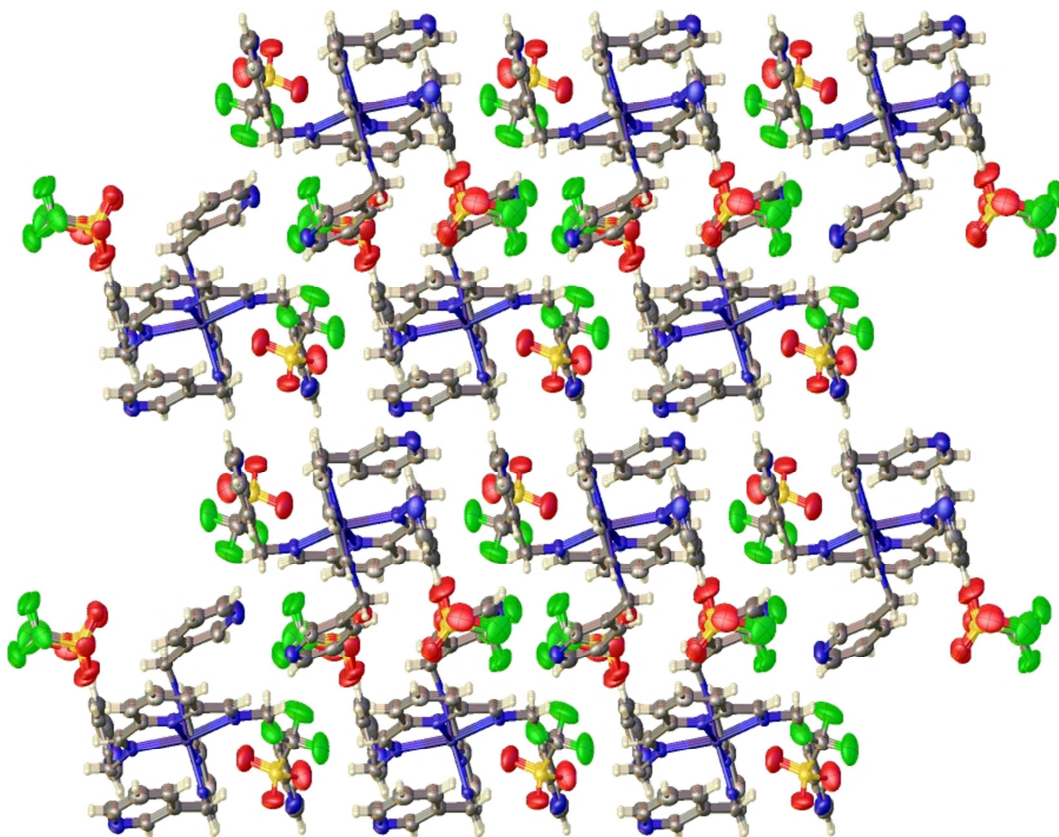

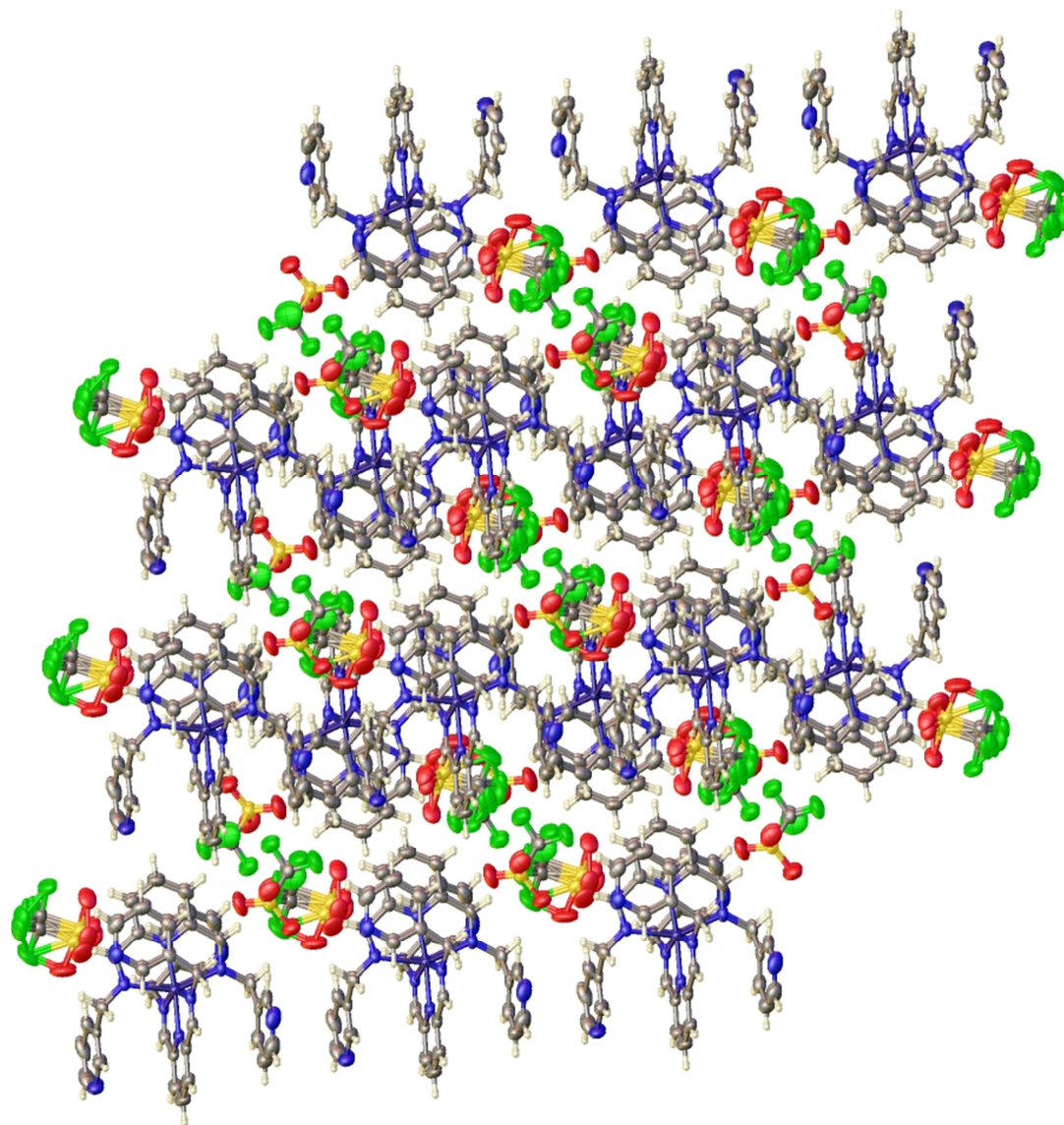Fig. 3S. Packing of $\mathbf{1}_2Zn^{2+}$ along b

Fig. 4S. Packing of $\mathbf{1}_2Zn^{2+}$ along c

Crystal structure of $[\mathbf{1}Ag^+]_n$: In the $[\mathbf{1}Ag^+]_n$ structures two ligands $\mathbf{1}$ and the Ag^+ metal ions form the dimeric self-complimentary molecular clefts, each $[\mathbf{1}M^+]$ 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.
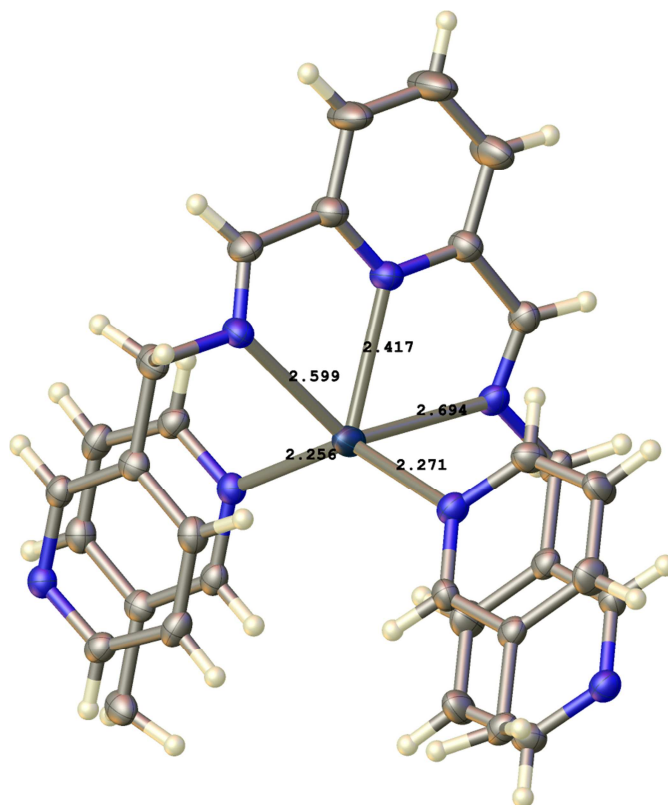
Fig. 5S. Coordination sphere of Ag^+ in $[1Ag^+]_n$ (uncoordinating residues have been omitted for clarity)
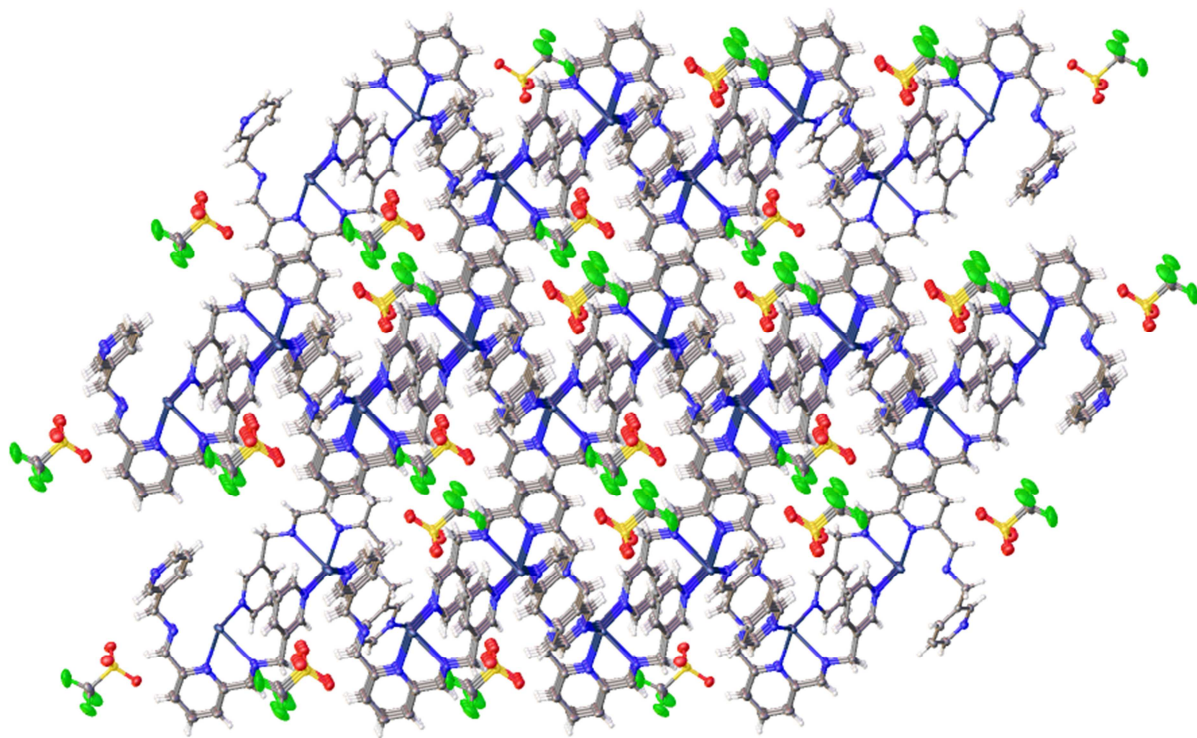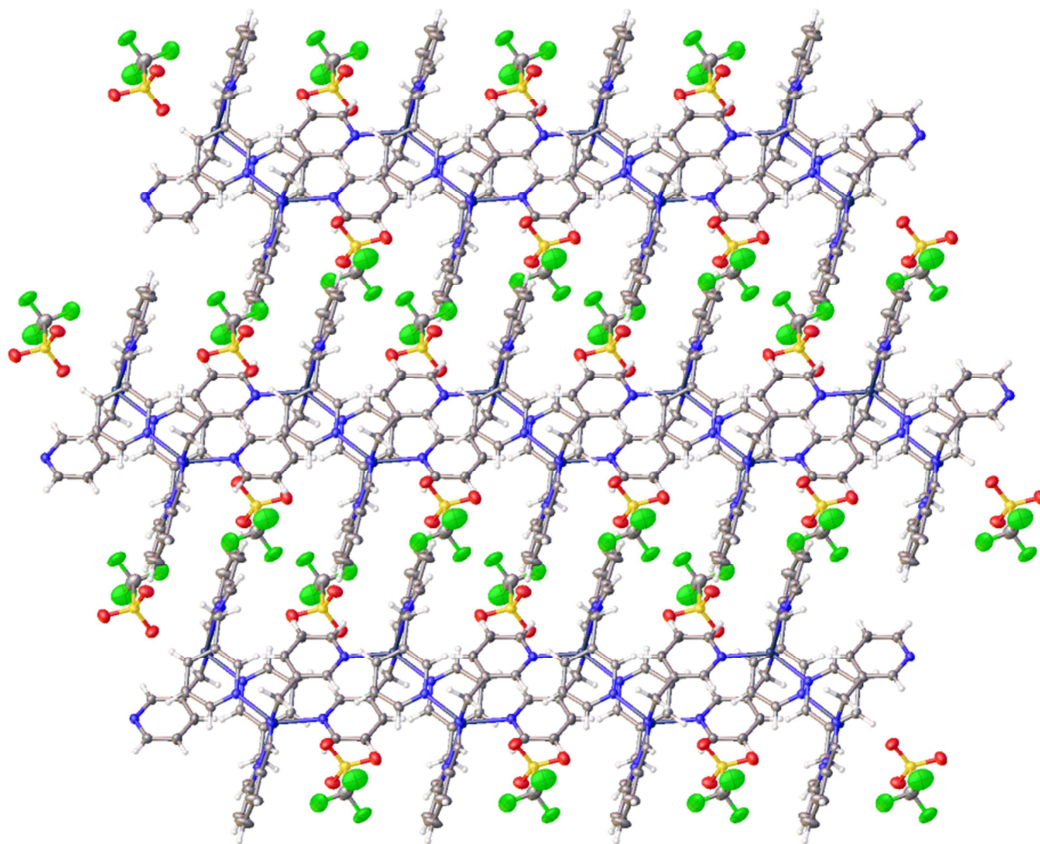
Fig. 6S. Packing of [**1**Ag$^+$]$_n$ along *a*

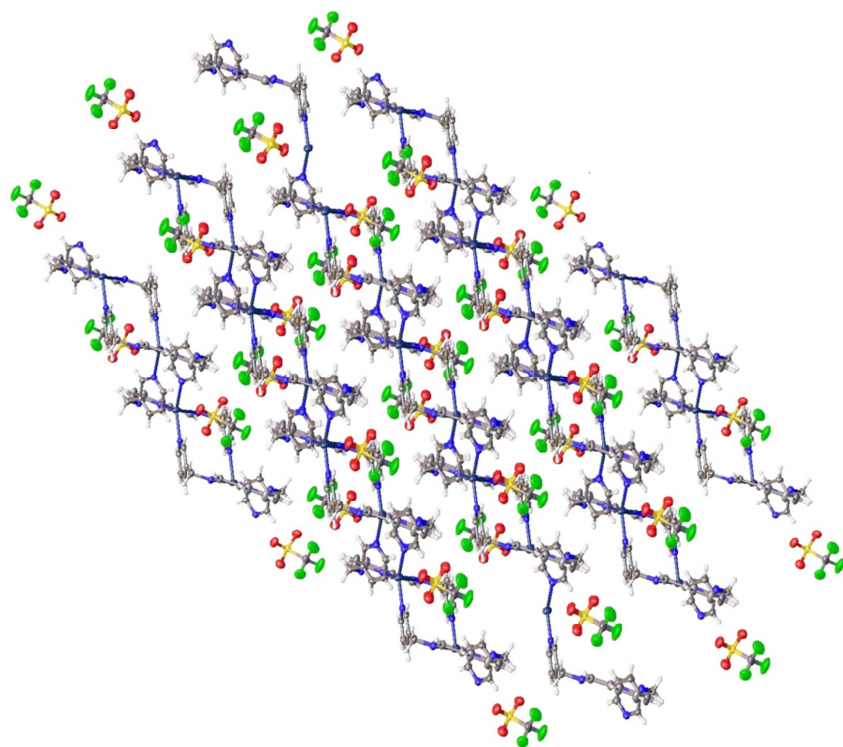
Fig. 7S. Packing of [**1**Ag$^+$]$_n$ along *b*

Fig. 8S. Packing of [**1**Ag$^+$]$_n$ along c

Crystal structure of [**1**Cu^{2+}]$_2$: Structure [**1**Cu^{2+}]$_2$ has two distinc types of Cu^{2+} ions. In both cases the copper cation presents an octahedral coordination sphere. Ligands **1** and Cu^{2+} metal ions form the dimeric self-complimentary molecular clefts, each [**1**M$^+$] entity being slotted into the other. The Cu^{2+} cations are coordinated by one terpy unit of the ligand **a** (the average 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.
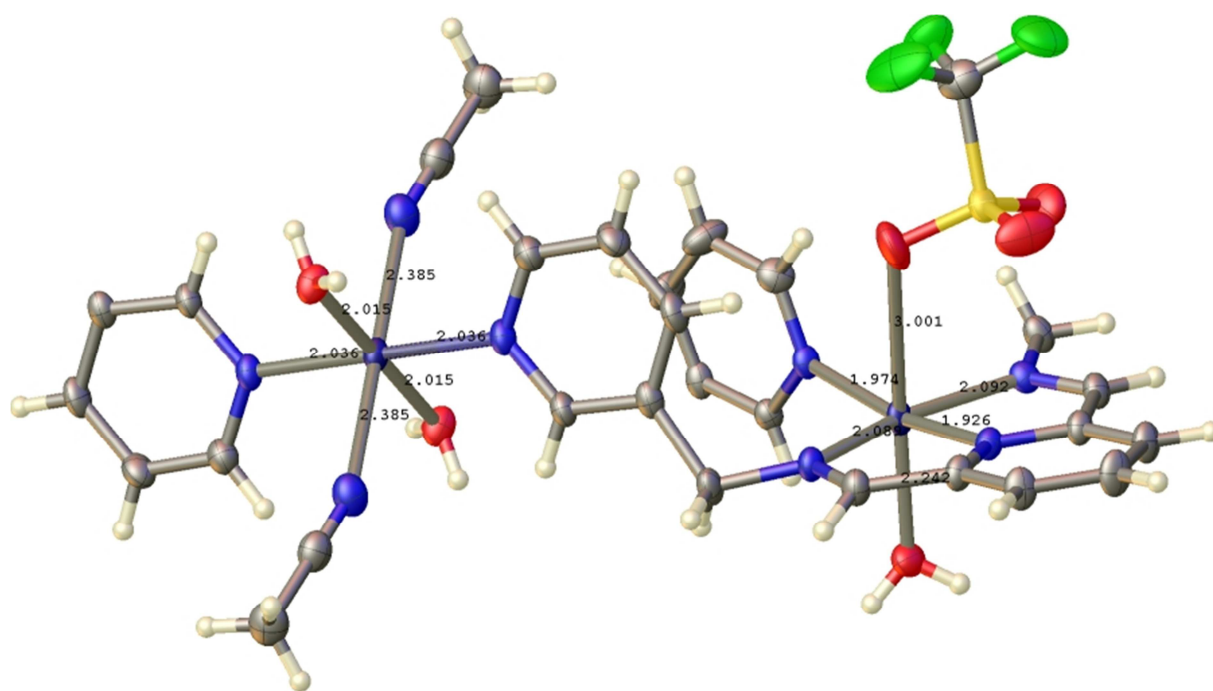
Fig. 9S. Coordination sphere of Cu^+ in $[\mathbf{1}Cu^{2+}]_2$ (uncoordinating residues have been omitted for clarity)
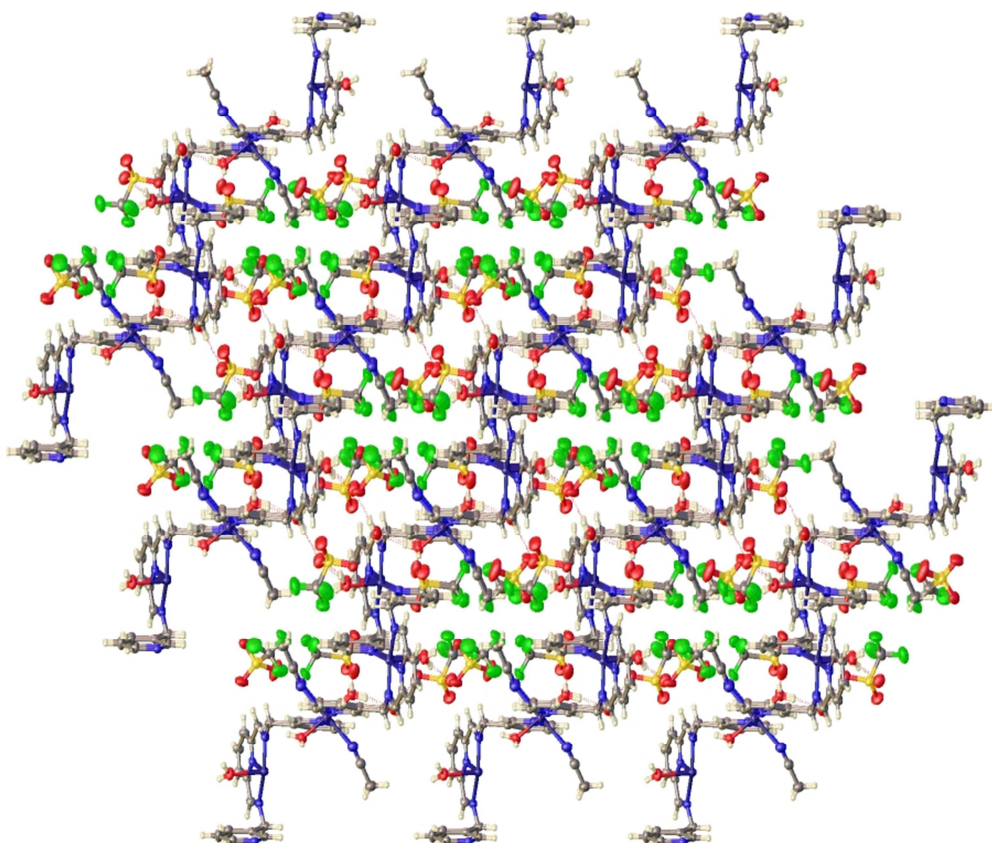
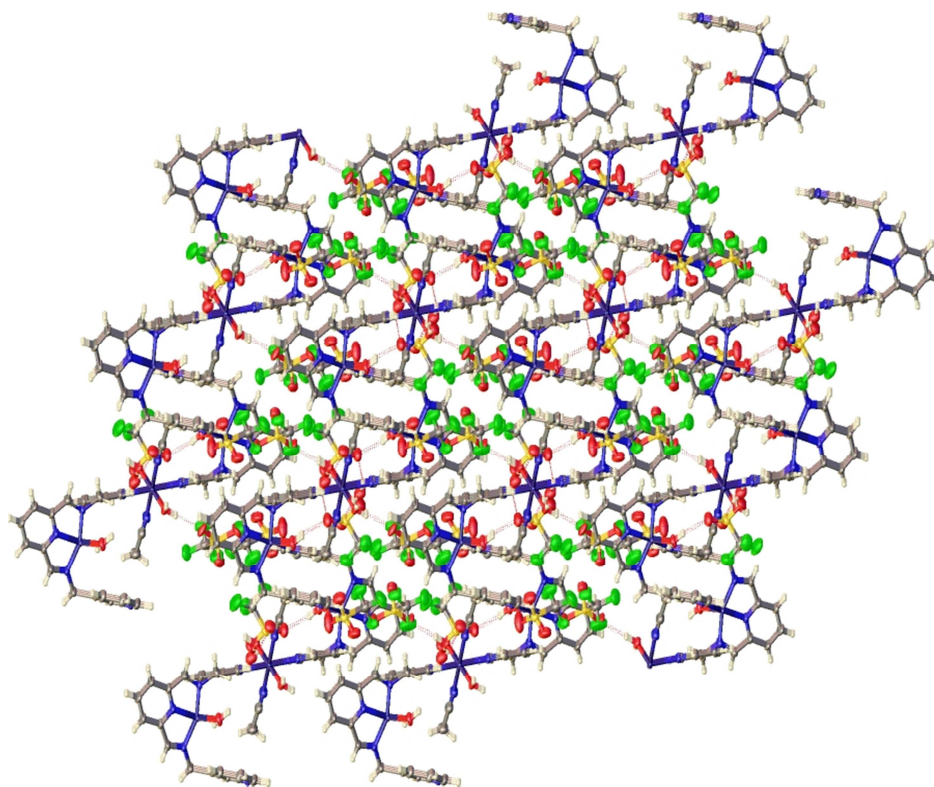Fig. 10S. Packing of [$\mathbf{1}$Cu^{2+}]$_2$ along *a*
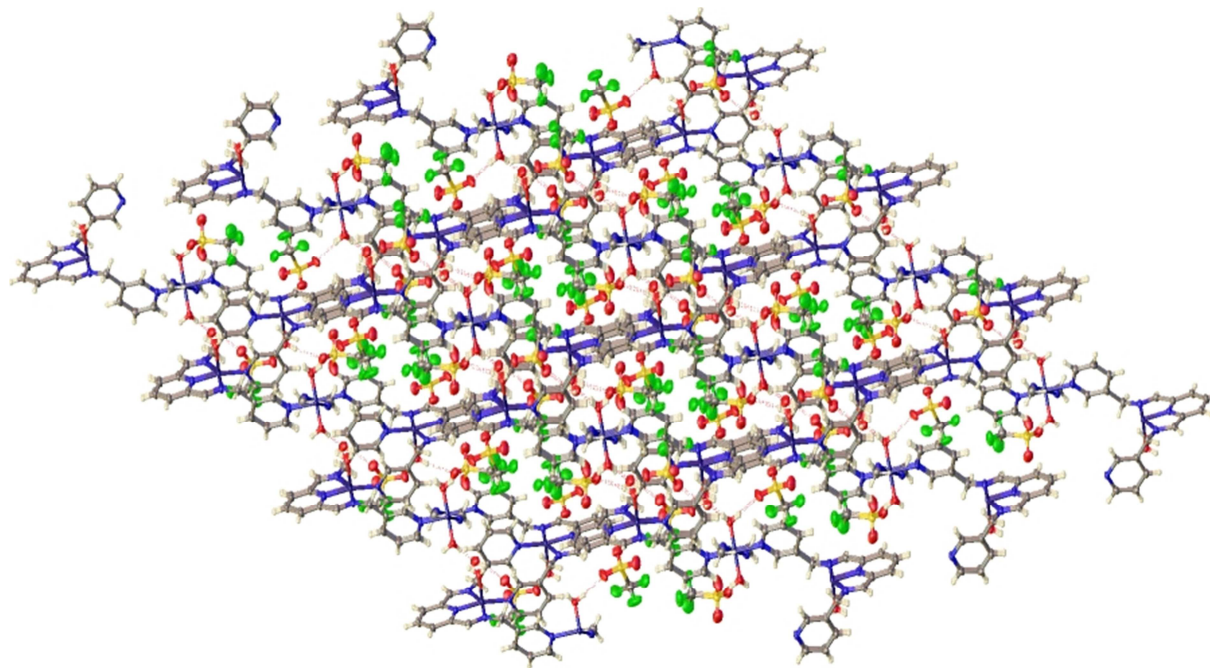
Fig. 11S. Packing of [$\mathbf{1}$Cu^{2+}]$_2$ along *b*

Fig. 12S. Packing of [$\mathbf{1}$Cu^{2+}]$_2$ along *c*

Crystal structure of 1_2Pb^{2+}: The X-ray structural analysis of 1_2Pb^{2+} crystals reveals the Pb^{2+} cations being coordinated by three ligands of **1,** two forming a cleft (average d_{Pb}^{2+}-$_{NPyridine}$= 2.630 Å of and d_{Pb}^{2+}-$_{Nimine}$= 2.755 Å) and pyridyl group from a third connecting adjacent complex (d_{Pb}^{2+}-$_{NPyridine}$= 2.847 Å). and one triflate anion (d_{Pb}^{2+}-$_{OTrif}$= 2.757 Å). It should be noted that while the d_{Pb}^{2+}-$_{NPyridine}$ distance varies only by approximately 0.2 Å, the d_{Pb}^{2+}-$_{Nimine}$ distances vary by about 0.4 Å. In the crystal the communication between 1_3Pb^{2+} duplexes is realized via the supplementary coordinative interaction by the pyridine side arm of the neigboring 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.
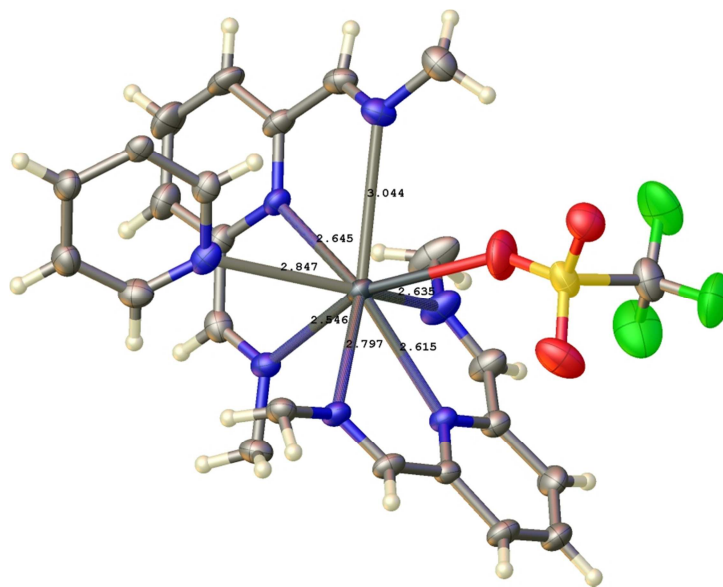

Fig. 13S. Coordination sphere of Pb^{2+} in 1_2Pb^{2+} (uncoordinating residues have been omitted for clarity)
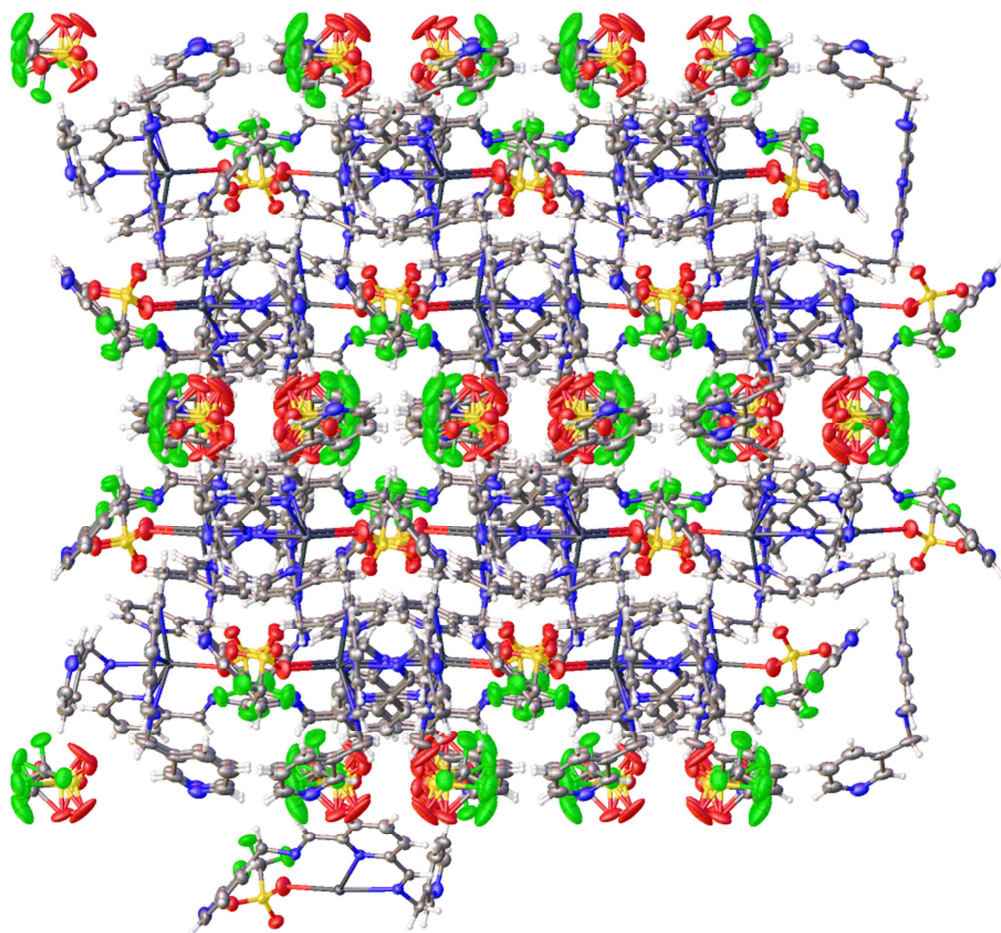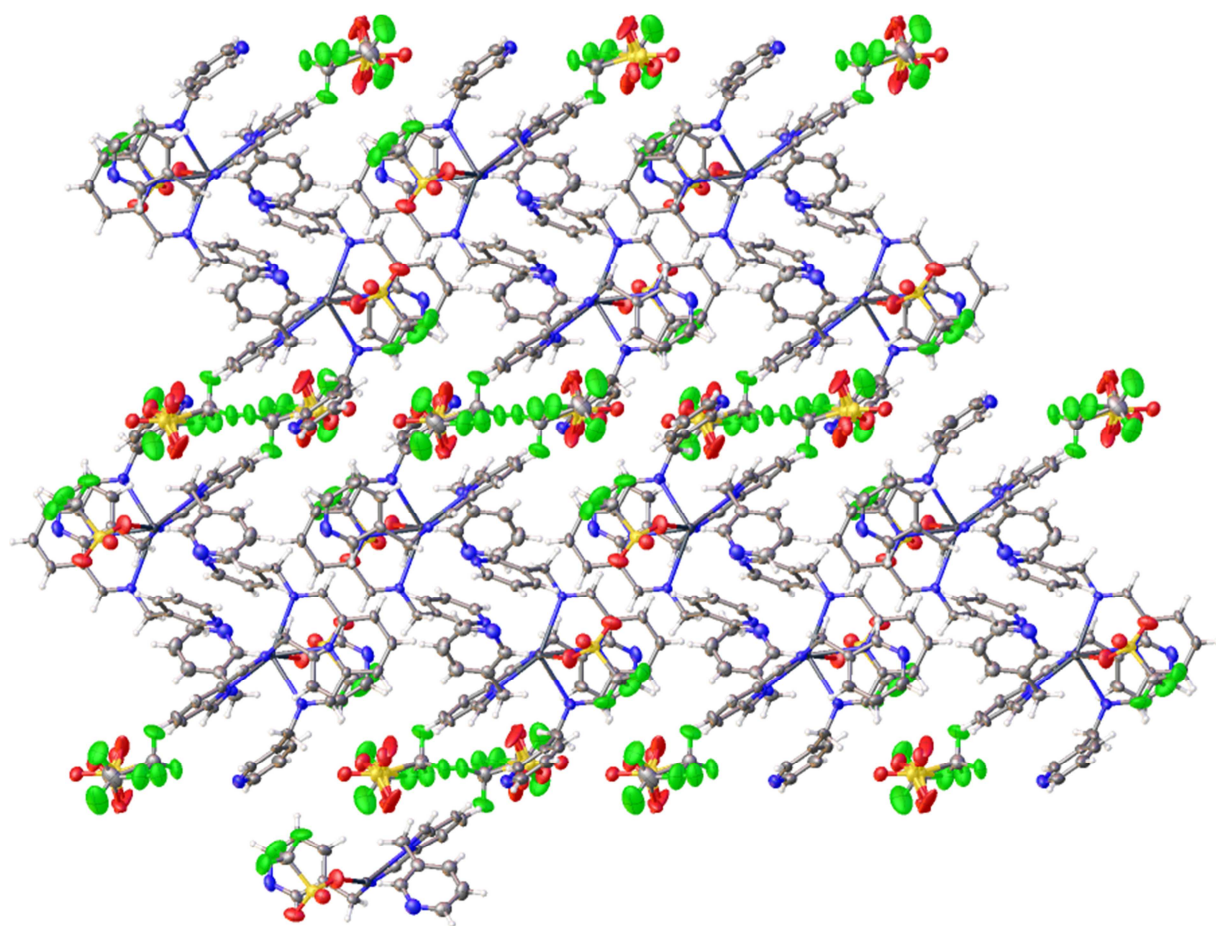
Fig. 14S. Packing of $\mathbf{1}_2\text{Pb}^{2+}$ along a

Fig. 15S. Packing of $\mathbf{1}_2Pb^{2+}$ along b
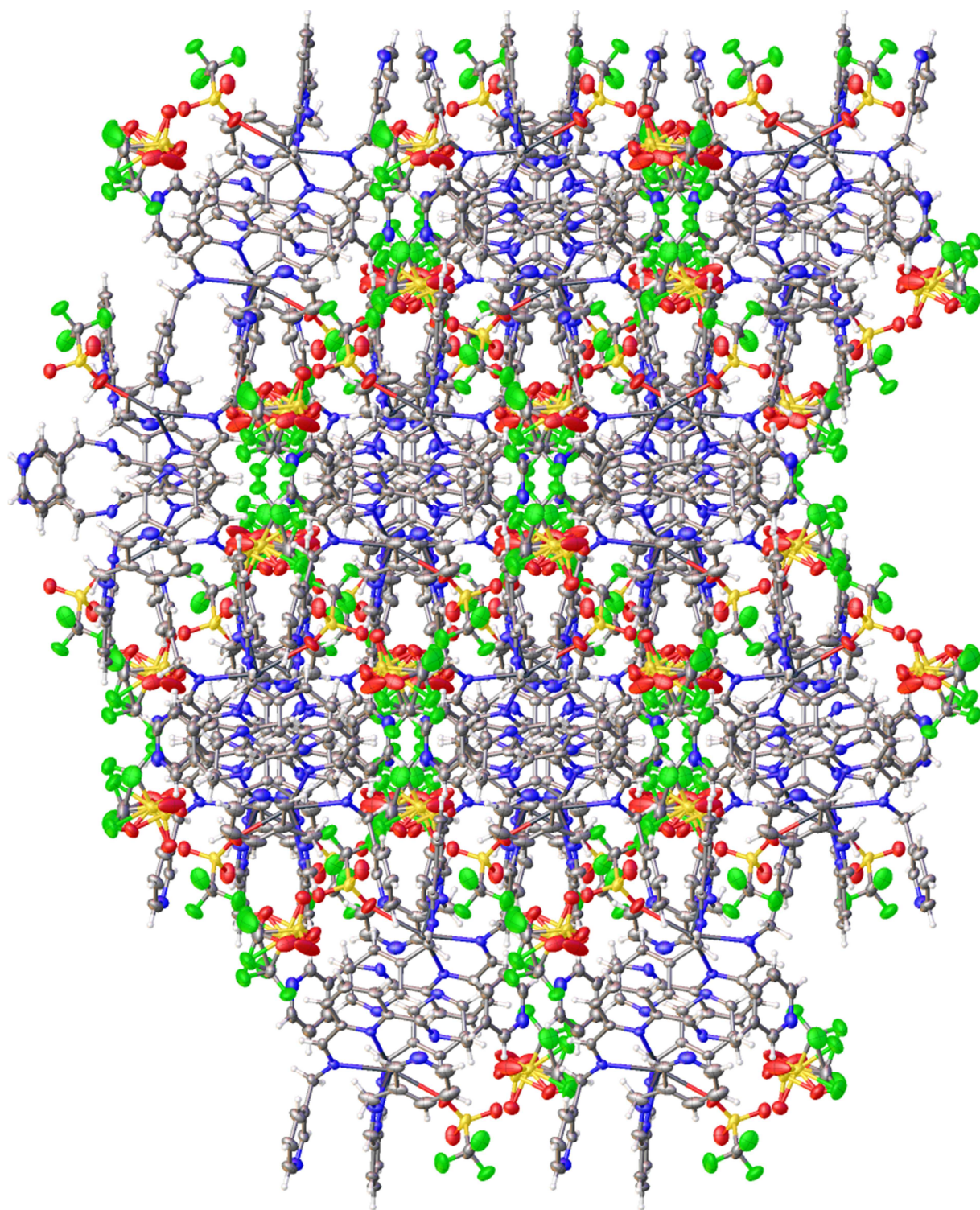
Fig. 16S. Packing of $\mathbf{1}_2Pb^{2+}$ along c

Crystal structure of $\mathbf{2}_2Zn^{2+}$: 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 $Zn(CF_3SO_3)_2$ and $Ag(CF_3SO_3)$ in CD_3CN. 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 $Zn(CF_3SO_3)_2$ and $Ag(CF_3SO_3)$ has been added in CD_3CN.
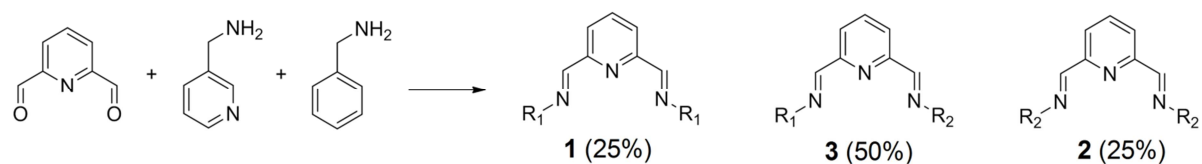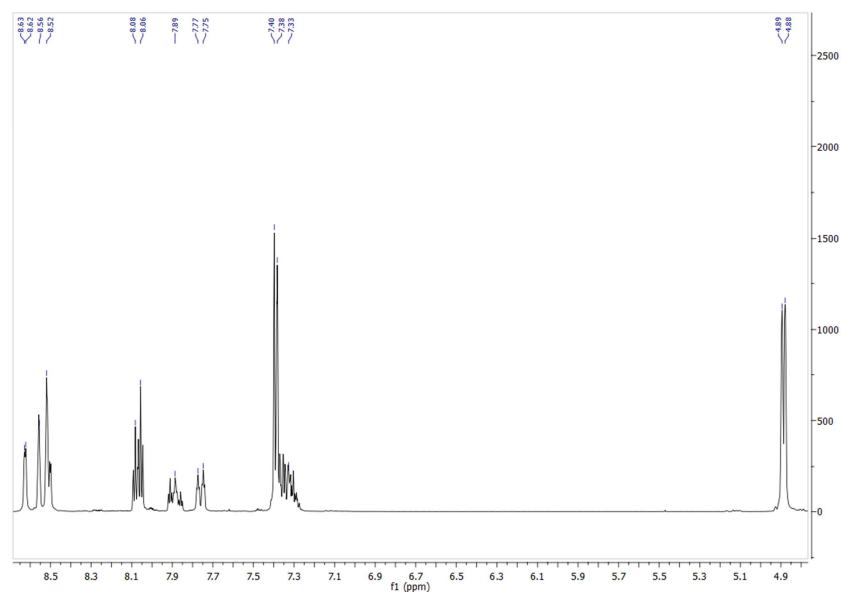

Scheme 1S.

Figure 17S. ^{1}H-NMR spectra section in CD_3CN 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

	Reaction		Metal			Solution	Crystal
1	AL	R1	0.5 Eq Zn			1_2Zn^{2+}	1_2Zn^{2+}
2	AL	R1	1 Eq Zn			$1Zn^{2+}$	1_2Zn^{2+}
3	AL	R1	0.5 Eq Ag			1_2Ag^+	$[1Ag^+]_n$
4	AL	R1	1 Eq Ag			$[1Ag^+]_n$	$[1Ag^+]_n$
5	AL	R1	0.5 Eq Zn	0.5 Eq Ag		1_2Zn^{2+}	1_2Zn^{2+}
6	AL	R1	0.5 Eq Zn	0.5 Eq Pb		1_2Zn^{2+}	1_2Zn^{2+}
7	AL	R1	0.5 Eq Pb	0.5 Eq Ag		**pp**	**-**
8	AL	R1	0.5 Eq Pb	0.5 Eq Ag	0.5 Eq Zn	1_2Zn^{2+}	1_2Zn^{2+}
9	AL	R1	1 Eq Zn	1 Eq Ag		$1Zn^{2+}$	-
10	AL	R2	0.5 Eq Zn			2_2Zn^{2+}	2_2Zn^{2+}
11	AL	R2	1 Eq Zn			2_2Zn^{2+}	2_2Zn^{2+}
12	AL	R2	0.5 Eq Ag			$Ag(L2)_2$	-
13	AL	R2	1 Eq Ag			$Ag(L2)$	-
14	AL	R2	0.5 Eq Zn	0.5 Eq Ag		2_2Zn^{2+}	2_2Zn^{2+}
15	AL	R2	1 Eq Zn	1 Eq Ag		2_2Zn^{2+}	2_2Zn^{2+}
16	AL	R1	R2	0.5 Eq Zn		mix	2_2Zn^{2+}
17	AL	R1	R2	1 Eq Ag		mix	$[1Ag^+]_n$

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).

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