Electronic Supporting Informations for Constitutional self-sorting of homochiral supramolecular helical singlecrystals from achiral components

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Materials and Methods: All reagents were obtained from Aldrich 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 CDCl₃ with the use of the residual solvent peak as reference. The assignments were made on the base of the COSY and NOESY spectra. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform 2+). Samples were continuously introduced into the mass spectrometer through a Waters 616HPLC pump. The temperature (60 °C) and the extraction cone voltage (V_c=5-10V) were usually set to avoid fragmentations.

Synthesis of ligands 1-5: Ligands 1^{4S} , 2^{5S} and 5^{6S} were synthesised as previously described in literature. For ligands 3 and 4: 2,6-Pyridinedicarboxaldehyde and 3F-anilines or 4-Faniline (1:2 mol : mol) were refluxed 2 hours in 20 mL of ethanol or toluene with stirring to give a clear solution. The solvent was concentrated and the ligands 3 or 4 recrystallized from acetonitrile as the pure white powders.

The solutions of all ligands 1-5, in CDCl₃ or CD₃CN give sharp ¹H NMR spectra with a strong deshielding of meta protons of the central pyridine ring, consistent with the *transoid* conformation of the -N=C-C=N- moiety. As expected a strong deshielding is observed for *meta* pyridine hydrogens, indicating a tight contact with the neighboring imine nitrogen atoms; this effect agrees with an unwrapped conformation of compounds 1-5 (W-shaped *transoid*, *transoid* form of the free ligand see ref 15 for details).

Synthesis of $1_2Zn^{2+}-5_2Zn^{2+}$, 1_2Fe^{2+} and 1_2Co^{2+} complexes The reactions were performed typically on a 10 mg scale of ligand. The ligands 1-5 and $Zn(CF_3SO_3)_2$, $Co(BF_4)_2$ or $Fe(BF_4)_2$ were dissolved in CD₃CN (1 mL), and stirred overnight at 40 °C. Layering such solutions of complexes $1_2Zn^{2+}-5_2Zn^{2+}$, 1_2Fe^{2+} and 1_2Co^{2+} in acetonitrile with the *i*-propylether at room temperature, resulted in a unique set of single-crystals suitable for X-ray single-crystal experiments.

 1_2 Zn²⁺: ¹H-NMR (CD₃CN, ppm) : δ = 8.823 (s, 4H, CH=N), 8.608-8.556 (t, 2H, H^a, J=7.8 Hz), 8.274-8.248 (d, 4H, H^b, J=7.8 Hz), 7.381-7.254 (m, 12H, H^{ar}, J=8.7 Hz), 6.912-6.884 (d, 8H, H^{ar}, J=3.35Hz). ES-MS: m/z (%): 317.7 (100)

 2_2 Zn²⁺: ¹H-NMR (CD₃CN, ppm) : δ = 8.689 (s, 4H, CH=N), 8.596-8.544 (t, 2H, H^a, J=7.8 Hz), 8.206-8.18 (d, 4H, H^b, J=7.8 Hz), 7.598 (s, 4H, OH), 6.656 (s, 16H, H^{ar}). ES-MS: m/z (%): 349.54 (100)

3₂Zn²⁺: ¹H-NMR (CDCl₃, ppm) : δ = 8.678 (s, 2H, CH=N), 8.302-8.276 (d, 2H, H^b), 7.988-7.936 (t, 1H, H^a), 7.377-7.319 (d, 4H, H^{arom}), 7.176-7.108 (d, 4H, H^{arom}). ES-MS: m/z (%): 353.5 (100)

 4_2 Zn²⁺: ¹H-NMR (CD₃CN, ppm) : δ= 8.812 (s, 4H, CH=N), 8.655-8.603 (t, 2H, H^a, J=7.8 Hz), 8.324-8.298 (d, 4H, H^b, J=7.8 Hz), 7.072-6.990 (m, 8H, H^{ar}), 6.857-6.788 (m, 8H, H^{ar}). ES-MS: m/z (%): 353.5 (100)

5₂Zn²⁺: ¹H-NMR (CD₃CN, ppm) : δ= 8.734 (s, 4H, CH=N), 8.608-8.556 (t, 2H, H^a, J=7.8 Hz), 8.227-8.201 (d, 4H, H^b, J=7.8 Hz), 6.804-6.715 (m, 16H, H^{arom}), 3.773 (s, 12H, OCH₃). ES-MS: m/z (%): 377.33 (100)

 1_2 Fe²⁺: ES-MS: m/z (%): 313.63 (100)

1₂Co²⁺: ES-MS: m/z (%): 314.69 (100)

Solid state structures of the Me²⁺ (Zn²⁺, Co²⁺ Pb²⁺) metallosupramolecular double standed helicates 1_2 Zn²⁺, 1_2 Fe²⁺ and 1_2 Co²⁺: The crystal structures of the complexes 1_2 Zn²⁺, 1_2 Fe²⁺ and 1_2 Co²⁺ formed by ligand 1 with Zn²⁺ Co²⁺ or Pb²⁺ ions, were determined from crystals obtained from a 1/1 acetonitrile/*i*-propylether solutions at room temperature.



Fig.1S. a, Crystal structure in stick representation; **b**, coordination octahedral geometry distances and **c**, superposed geometries of the complexes $1_2 Zn^{2+}$ (red) , $1_2 Fe^{2+}$ (blue) and $1_2 Co^{2+}$ (green). The Zn^{2+} , Fe^{2+} and Co^{2+} ions are shown as gray blue and pink spheres, respectively.

The X-ray structural determinations of the pale-yellow 1_2Zn^{2+} , violet 1_2Fe^{2+} and pink 1_2Co^{2+} single-crystals revealed that the complexes present approximately the same structure: self-complementary mononuclear complexes, which self-assemble in the solid state as intriguing coordination polymers with an unprecedented architecture resulting from the crossover of the orthogonal-pseudo-terpyridine complexation and π - π stacking and van der Waals interactions between the peripheral phenyl groups. The molecular and the crystal packing structures are presented in Figure 1Sa-c.

X-ray Single Crystal Diffraction Data for $1_2Zn^{2+}-5_2Zn^{2+}$, 1_2Fe^{2+} and 1_2Co^{2+} complexes: The diffraction intensities were collected at 173 K using an Oxford Diffraction Xcalibur-I and a Gemini-S diffractometer. The crystal-to-detector distance was 50 mm for all measurements. The structures were solved by direct methods using SIR2002^[1S] or by abinitio (charge-flipping) methods using SUPERFLIP^[2S] and refined by least-squares methods on F using CRYSTALS^[3S], against |F| on data having $I>2\sigma(I)$; *R*-factors are based on these data. The absolutes structures were assigned on the basis of the Flack x parameter (x is the fractional contribution of the inverted component of a racemic twin; it is expected to be zero for a correct structure, unity for the inverted structure). CCDC 695908-695913 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

The unit cell of the complex 1_2Zn^{2+} was found to contain four complexes together with eight triflate counterions and four acetonitrile molecules. Crystal dimensions: 0.17x0.25x0.38mm, cell dimensions: a=8.2081(3)Å, b=14.5003(5)Å, c=18.7227(7)Å, $\alpha=90^{\circ}$, $\beta=90^{\circ}$, $\gamma=90^{\circ}$, V=2228.37(14)Å³, orthorhombic, space group $P22_12_1$, Z=4, $\rho_{calcd}=1.515$ gcm⁻³, $\mu=0.728$ mm⁻¹. 42552 measured reflections, 7222 unique, 5195 with $I>2\sigma(I)$. $R_{int}=0.077$ Final R factors $R_1=0.0362$ and $wR_2=0.0387$; Flack parameter^[7S]=0.000(9), 304 parameters, 0 restraints, maximal residual electron density is 0.53 eÅ⁻³.

The unit cell of the complex 1_2 Fe²⁺ was found to contain eight complexes together with sixteen tetrafluoroborate counterions and four acetonitrile molecules. Crystal dimensions: 0.09x0.11x0.19mm, cell dimensions: a=8.1717(5)Å, b=46.7421(2)Å, c=29.9558(4)Å, $\alpha=90^{\circ}$, $\beta=101.11(2)^{\circ}$, $\gamma=90^{\circ}$, V=7479.5(7)Å³, monoclinic, space group $P2_1$ /c, Z=4, $\rho_{calcd}=1.474$ gcm⁻³, $\mu=0.484$ mm⁻¹. 46072 measured reflections, 19550 unique, 3803 with $I>2\sigma(I)$. $R_{int}=0.061$.

Final *R* factors R_1 =0.0973 and wR_2 =0.0679; 457 parameters, 0 restraints, maximal residual electron density is 1.04 eÅ⁻³. The data are rather weak data, because of rather small crystal and rather large mosaicity. Only Fe atoms were refined anisotropically.

The unit cell of the complex 1_2 Co²⁺ was found to contain six complexes together with twelve tetrafluoroborate counterions. Crystal dimensions: 0.15x0.21x0.27mm, cell dimensions: a=12.4612(5)Å, b=15.4657(7)Å, c=21.0453(9)Å, $\alpha=90^{\circ}$, $\beta=90^{\circ}$, $\gamma=90^{\circ}$, V=4055.9(3)Å³, orthorhombic, space group *Pbcb*, Z=4, $\rho_{calcd}=1.443$ gcm⁻³, $\mu=0.501$ mm⁻¹. 78751 measured reflections, 6892 unique, 1859 with $I>2\sigma(I)$. $R_{int}=0.051$. Final *R* factors $R_1=0.0338$ and $wR_2=0.0360$; 281 parameters, 8 restraints, maximal residual electron density is 0.53 eÅ⁻³.

The unit cell of the complex $2_2 Zn^{2+}$ was found to contain four complexes together with eight triflate counterions and eight acetonitrile molecules. Crystal dimensions: 0.05x0.20x0.48mm, cell dimensions: a=25.5260(2)Å, b=8.2795(5)Å, c=23.826(2)Å, $\alpha=90^{\circ}$, $\beta=113.137(6)^{\circ}$, $\gamma=90^{\circ}$, V=4630.4(6)Å³, monoclinic, space group $P2_1/c$, Z=4, $\rho_{calcd}=1.548$ gcm⁻³, $\mu=0.142$ mm⁻¹. 87879 measured reflections, 15280 unique, 2117 with $I>2\sigma(I)$. $R_{int}=0.097$. Final *R* factors $R_1=0.0486$ and $wR_2=0.0554$; 290 parameters, 0 restraints, maximal residual electron density is 0.77 eÅ⁻³. All crystals were thin platelets and in addition weak scatterers; inspection of the diffraction images shows a rather high mosaicity. This leads to the overall low intensity and the low number of observed reflections

The unit cell of the complex $3_2 Zn^{2+}$ was found to contain four complexes together with eight triflate counterions. Crystal dimensions: 0.40x0.40x0.55mm, cell dimensions: a=10.0922(2)Å, b=20.3191(4)Å, c=22.3161(3)Å, $\alpha=114.401(1)^{\circ}$, $\beta=91.642(1)^{\circ}$, $\gamma=89.737(1)^{\circ}$, V=4165.62(13)Å³, triclinic, space group *P*-1, Z=2, $\rho_{calcd}=1.603$ gcm⁻³, $\mu=0.790$ mm⁻¹. 124395 measured reflections, 31833 unique, 21186 with *I*>2 σ (*I*). $R_{int}=0.023$. Final *R* factors $R_1=0.0489$ and $wR_2=0.0485$; 1171 parameters, 0 restraints, maximal residual electron density is 2.64 eÅ⁻³. One triflate counter-ion appeared to be slightly disordered, which explains the rather high residual density close to this anion. However, based on the Fourier difference densities, it was not possible to build an appropriate model explaining the disorder. The unit cell of the complex $4_2 Zn^{2+}$ was found to contain six complexes together with twelve triflate counterions and two acetonitrile molecules. Crystal dimensions: 0.10x0.15x0.25mm, cell dimensions: a=8.0917(1)Å, b=14.7056(2)Å, c=19.4187(3)Å, $\alpha=90^{\circ}$, $\beta=90^{\circ}$, $\gamma=90^{\circ}$, V=2310.70(6)Å³, orthorhombic, space group P22₁2₁, Z=4, $\rho_{calcd}=1.564$ gcm⁻³, $\mu=0.720$ mm⁻¹. 23066 measured reflections, 5334 unique, 4113 with $I>2\sigma(I)$. $R_{int}=0.031$. Final *R* factors $R_1=0.0288$ and $wR_2=0.0350$; Flack parameter⁷⁸=0.019(10) 322 parameters, 0 restraints, maximal residual electron density is 0.67 eÅ⁻³.

The unit cell of the complex $5_2 Zn^{2+}$ was found to contain two complexes together with four triflate counterions. Crystal dimensions: 0.30x0.40x0.50mm, cell dimensions: b=13.01212(3)Å, c=14.4037(3)Å, $\alpha=76.696(2)^{\circ}$, *a*=12.9994(3)Å, $\beta = 74.783(2)^{\circ}$, $\gamma = 88.948(2)^{\circ}$, V=2285.57(9)Å³, triclinic, space group P-1, Z=2, $\rho_{calcd} = 1.532$ gcm⁻³, $\mu = 0.718$ mm⁻¹. 23919 measured reflections, 12517 unique, 10261 with $I > 2\sigma(I)$. $R_{int}=0.011$ Final R factors R_1 =0.0789 and wR_2 =0.0998; 828 parameters, 583 restraints, maximal residual electron density is 2.47 eÅ⁻³. One triflate anion was found to be disordered within the oxygen and fluorine part, sharing the S-C skeletton. The two parts were regularized using the coordinates of the non-disordered triflate counter ion and refined using rigid body contraints and bond length restraints. The total occupancy of the two parts was fixed at 1.00. Equivalent isotropic temperature factors for the F and O atoms of each part were refined. Shift-limiting restraints were applied in order to stabilize the refinement of the disordered triflate anion. Despite this modelling rather large residuals are still found in the oxygen and fluorine parts of the disordered triflate counter anion.

In all structures the $Me^{2+} = Zn^{2+}$, Fe^{2+} and Co^{2+} ion are fully coordinated by two ligands arranged into two orthogonal planes and present an octahedral coordination geometry (Fig. 1Sa). Whereas the average $Zn^{2+}-N_{Pyridine}$ and $Co^{2+}-N_{Pyridine}$ distances are similar: 1.88 Å, the average $Fe^{2+}-N_{Pyridine}$ distance is much longer: 2.06 Å. The $Me^{2+}-N_{imine}$ distances are progressively increasing as following: $Zn^{2+}-N_{imine}$, $Co^{2+}-N_{imine}$ and $Fe^{2+}-N_{imine}$ distances of 2.00 Å, 2.12 Å and 2.25 Å, respectively (Fig.1Sb). These geometrical parameters are observed to be fairly different within this series and as expected the coordination behaviour leads to the slight differences in the spatial disposition of lateral phenyl arms. As an important consequence the 1_2Zn^{2+} , 1_2Fe^{2+} and 1_2Co^{2+} double helix complexes are not isostructural: they crystallize in different space groups ($P22_12_1$, $P2_1/c$ and Pbcb, respectively) and display very different unit cells and packing arrangements. The average $Zn^{2+}-N_{Pyridine}$ and $Zn^{2+}-N_{imine}$ distances of 2.04 Å and 2.24 Å respectively are both increasing in substituted $2_2Zn^{2+}-5_2Zn^{2+}$.



Figure 2S Crystal packing structure of the homochiral complex $1_2 Zn^{2+}$: **a**. side view and **b**. top-view in space-filling representation.



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Figure 3S Crystal packing structure of the heterochiral complex 1_2 Fe²⁺: **a**. side view in spacefilling of the 1_2 Fe²⁺ complexes presenting a half-tight stacking contact (average distance of 3.90 Å) and a half van der Waals contact (average distance of 5.67 Å) with a vicinal mononuclear. **b.** the half-stacked interface generate the mononuclear complexes interdigitation and chirality propagation (red-red mononuclear complexes interactions on the right); the half-open interface generate complex separation and chirality disruption (red-blue mononuclear complexes interactions on the left).



Figure 4S Crystal packing structure of the heterochiral complex 1_2 Co²⁺: **a**. top-view and **b**. side view in space-filling representation.



Figure 5S Crystal packing structure of the homochiral complex $2_2 Zn^{2+}$: **a**. top-view and **b**. side view in stick representation. The Zn^{2+} atoms are shown as blue spheres



Figure 6S Crystal packing structure of the homochiral complex $3_2 Zn^{2+}$: **a**. top-view in stick representation **b**. side view of simultaneous fluorine segregation of 4-*F*-phenyl and -CF₃ groups of triflate anions c. the mononuclear complexes interdigitation with chirality propagation and **d**. the mononuclear complexes separation via flurine segregation with chirality disruption between the double helical strands. The F atoms are shown as magenta spheres



Figure 7S Crystal packing structure of the homochiral complex $4_2 Zn^{2+}$: **a**. top-view in stick representation **b**. side view of internal fluorine segregation and of c. the mononuclear

complexes interdigitation and chirality propagation between the double helical strands. The F atoms are shown as magenta spheres



Fig. 8S Crystal packing structure of the heterochiral mononuclear complexes 5_2Zn^{2+} : side view in stick representation. The Zn^{2+} atoms are shown as blue spheres



Fig. 9S Side view in space-filling representation of the crystal packing of the mononuclear complexes: a, 2_2Zn^{2+} b, 3_2Zn^{2+} c, 4_2Zn^{2+} and d, 5_2Zn^{2+} .

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