Towards polymorphism control in coordination networks and metallo-organic salts

Christopher J. Adams, Amy L. Gillon, Matteo Lusi and A. Guy Orpen*

School of Chemistry, University of Bristol, Bristol BS8 1TS

Supplementary information

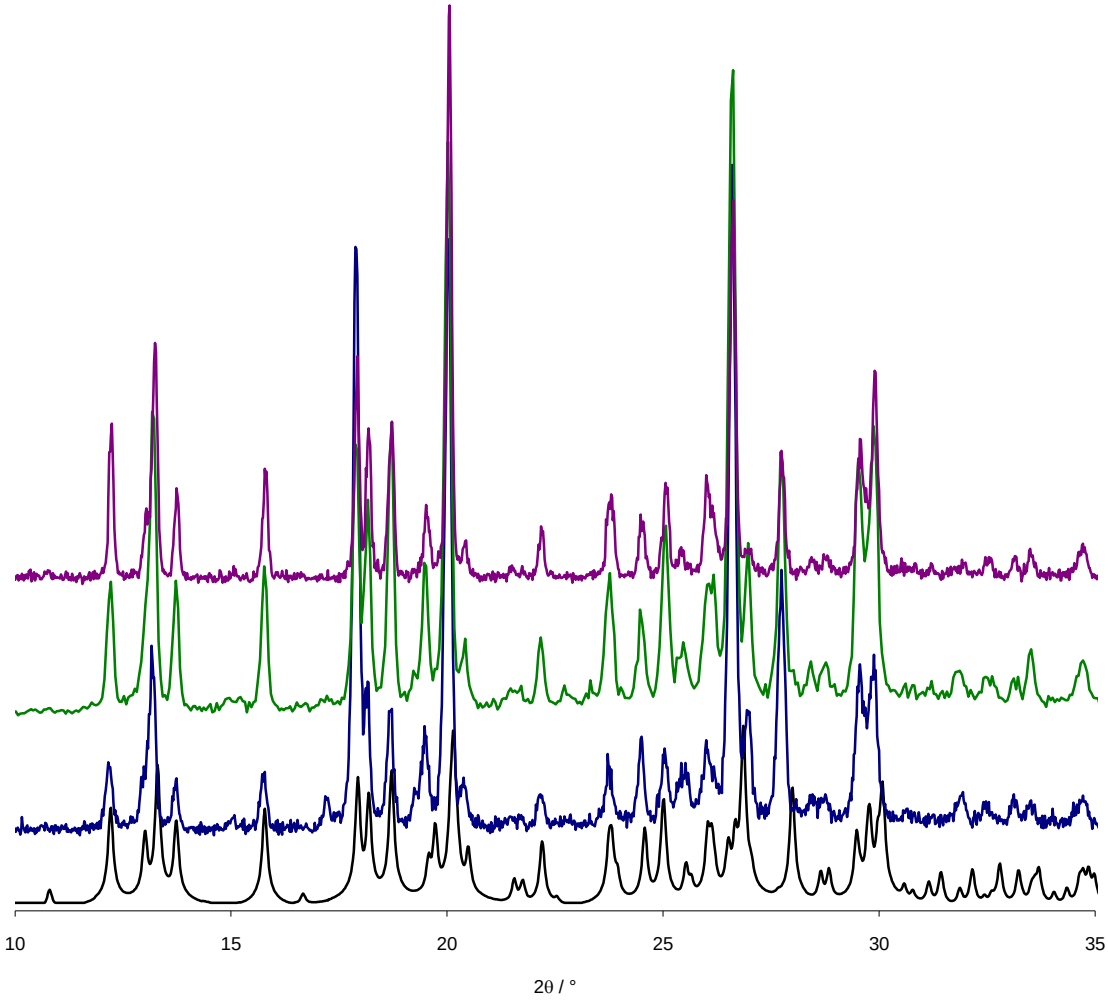

Figure S1: PXRD patterns for [4,4′-H_2bipy][$ZnCl_4$] **3**: calculated from the crystal structure (black); solution synthesis (blue, Scheme route (vi)); grinding synthesis (green, Scheme route (vii)); HCl absorption (purple, Scheme route (viii)).

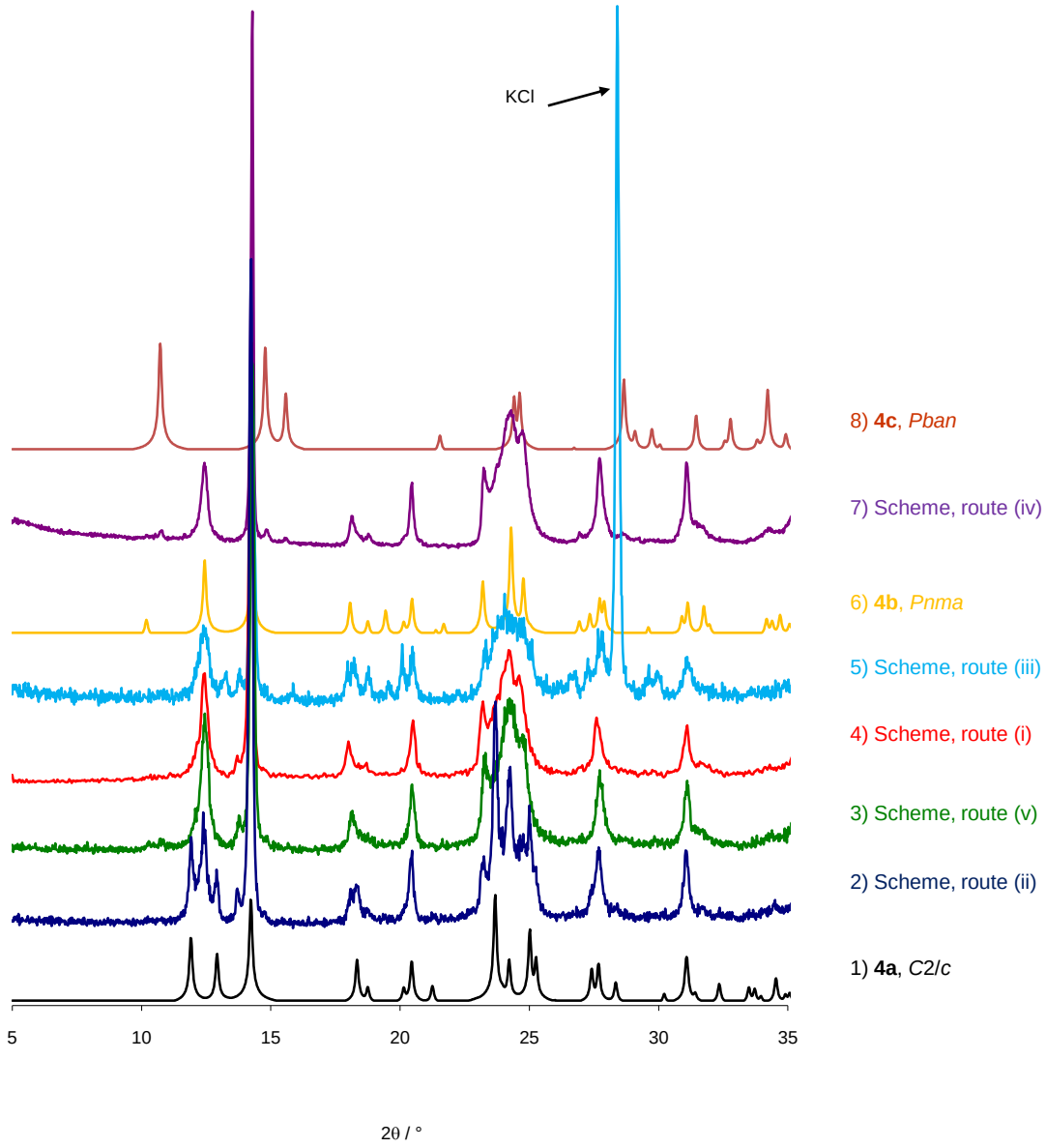

Figure S2: Comparison of the PXRD patterns calculated for the various polymorphs of **4** with those measured from the product obtained by various methods: 1) calculated for **4a** (black, *C2/c* phase); 2) solution synthesis (blue, Scheme route (ii)); 3) grinding (green, Scheme route (v)); 4) thermal elimination (red, Scheme route (i)); 5) mechanochemical elimination with KOH (light blue, Scheme route (iii)); 6) calculated for **4b** (yellow, *Pnma* phase); 7) By reaction of [4,4′-H_2bipy]Cl_2 with basic zinc carbonate (violet, Scheme route (iv)); 8) calculated for **4c** (brown, *Pban* phase).

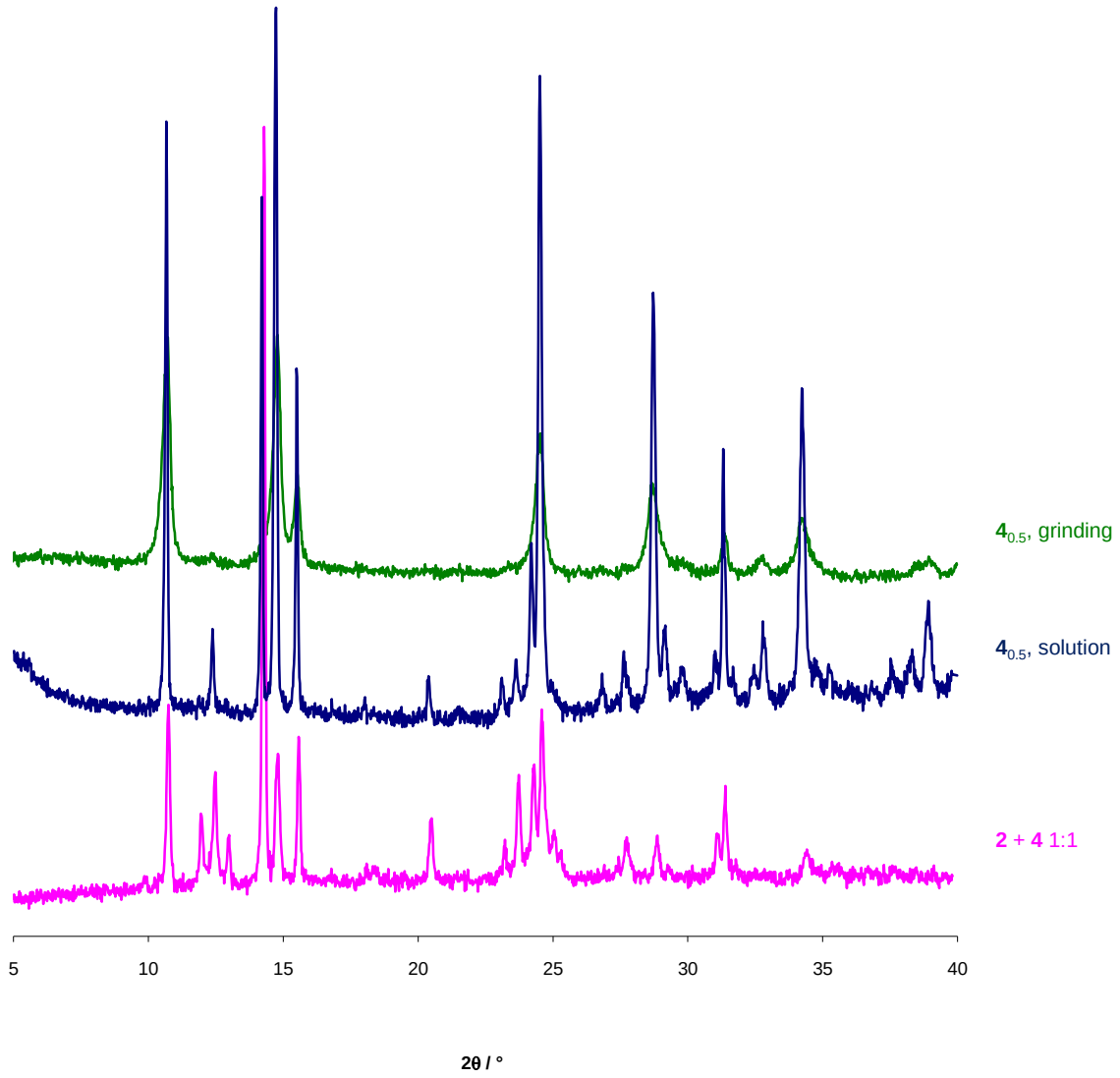

Figure S3: Comparison of PXRD patterns measured for different samples: mixing equivalent amounts of **2** and **4** obtained from solution (pink), containing all three phases; solution synthesis of $\mathbf{4_{0.5}}$ (blue), containing phases **4b** and **4c**; grinding synthesis of $\mathbf{4_{0.5}}$ (green), containing just **4c**.

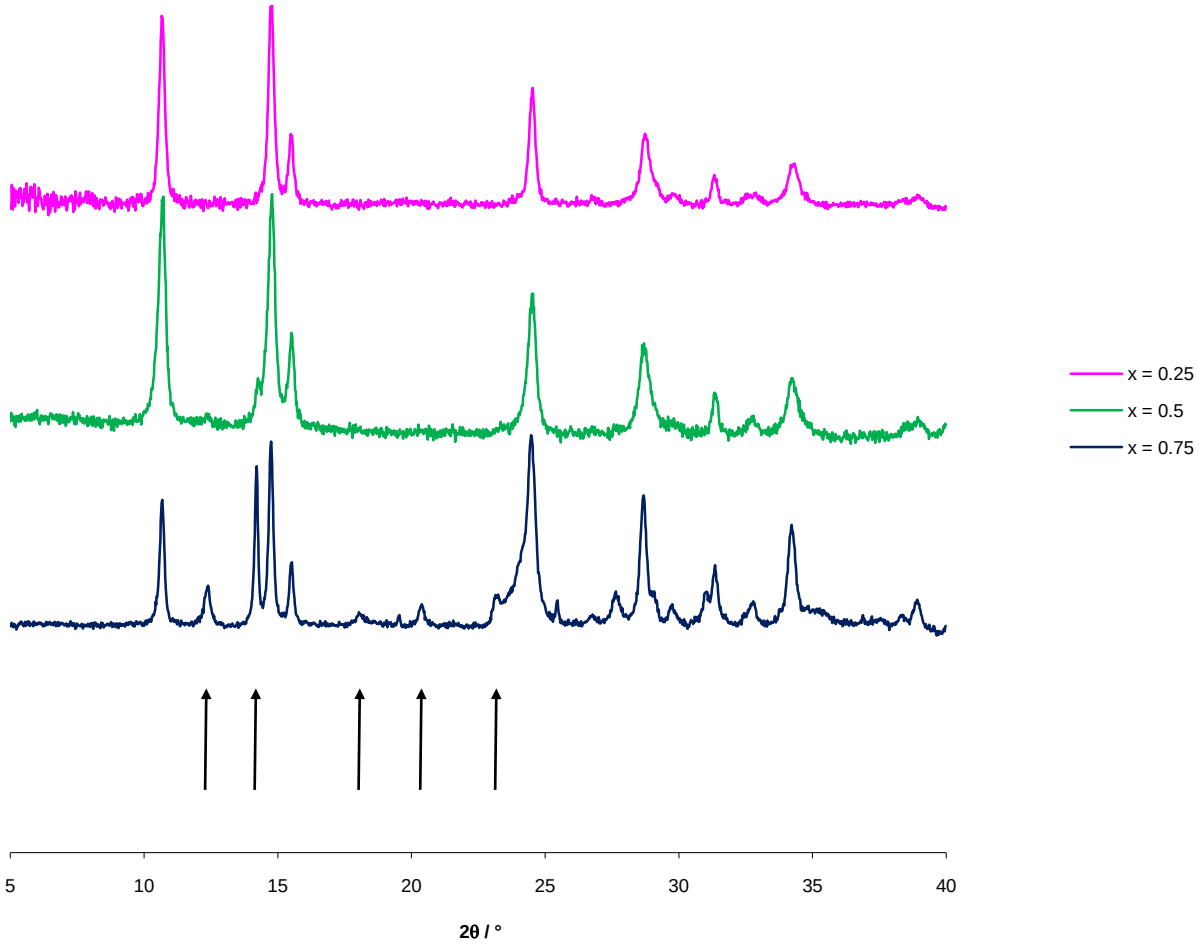

Figure S4: Comparison of PXRD patterns measured for $\mathbf{4_x}$ obtained by grinding 4,4′-bipy with cobalt and zinc chloride in a 1:3 ratio $\mathbf{4_{0.75}}$ (blue), in a 1:1 ratio $\mathbf{4_{0.5}}$ (green) and a 3:1 ratio $\mathbf{4_{0.25}}$ (pink). Peaks due to the tetrahedral *Pnma* polymorph **4b** are indicated by arrows, and others are due to the octahedral *Pban* polymorph **4c**.

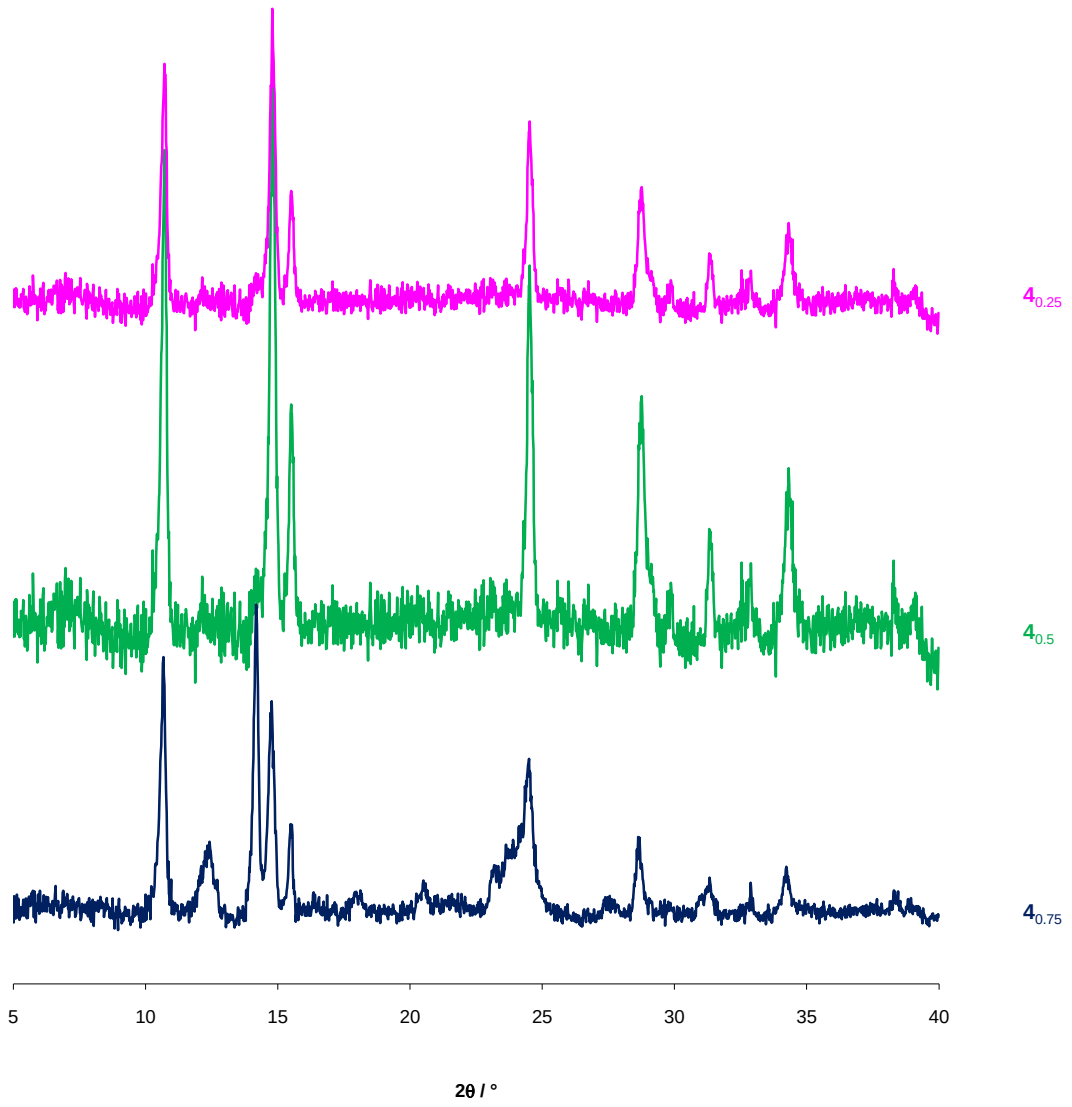

Figure S5: PXRD patterns for samples of [{(4,4′-bipy)$Co_{1-x}Zn_xCl_2$}$_n$] $\mathbf{4_x}$ obtained by thermal elimination from [4,4′-H_2bipy][$Co_{1-x}Zn_xCl_4$] $\mathbf{3_x}$: Co / Zn in 1:3 ratio $\mathbf{4_{0.75}}$ (blue); Co / Zn in 1:1 ratio $\mathbf{4_{0.5}}$ (green); Co / Zn in 3:1 ratio $\mathbf{4_{0.25}}$ (pink).

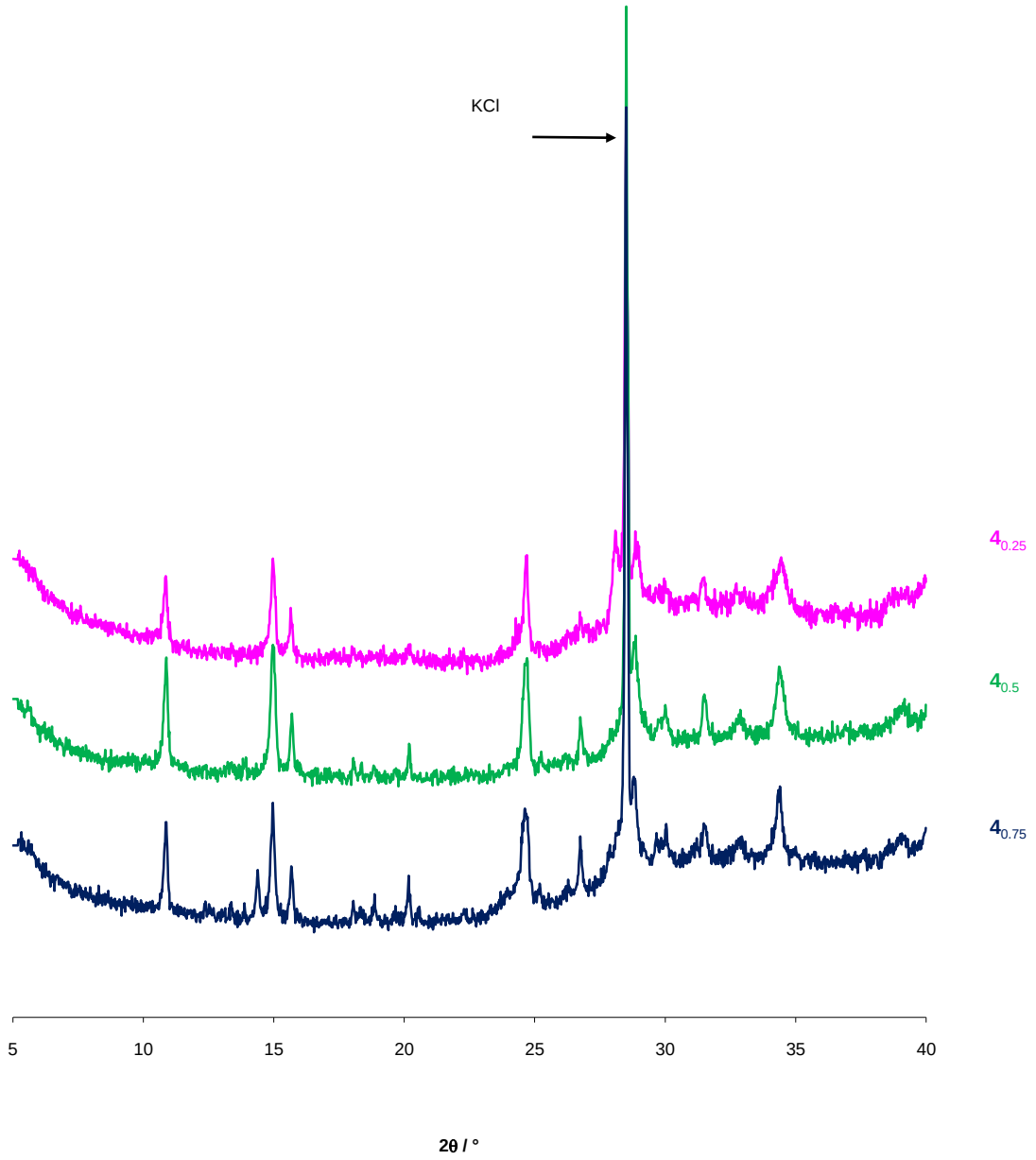

Figure S6: PXRD patterns for samples of [{(4,4′-bipy)$Co_{1-x}Zn_xCl_2$}$_n$] $\mathbf{4_x}$ obtained by mechanochemical elimination from [4,4′-H_2bipy][$Co_{1-x}Zn_xCl_4$] $\mathbf{3_x}$: Co / Zn in 1:3 ratio, $\mathbf{4_{0.75}}$ (blue); Co / Zn in 1:1 ratio, $\mathbf{4_{0.5}}$ (green); Co / Zn in 3:1 ratio, $\mathbf{4_{0.25}}$ (pink).

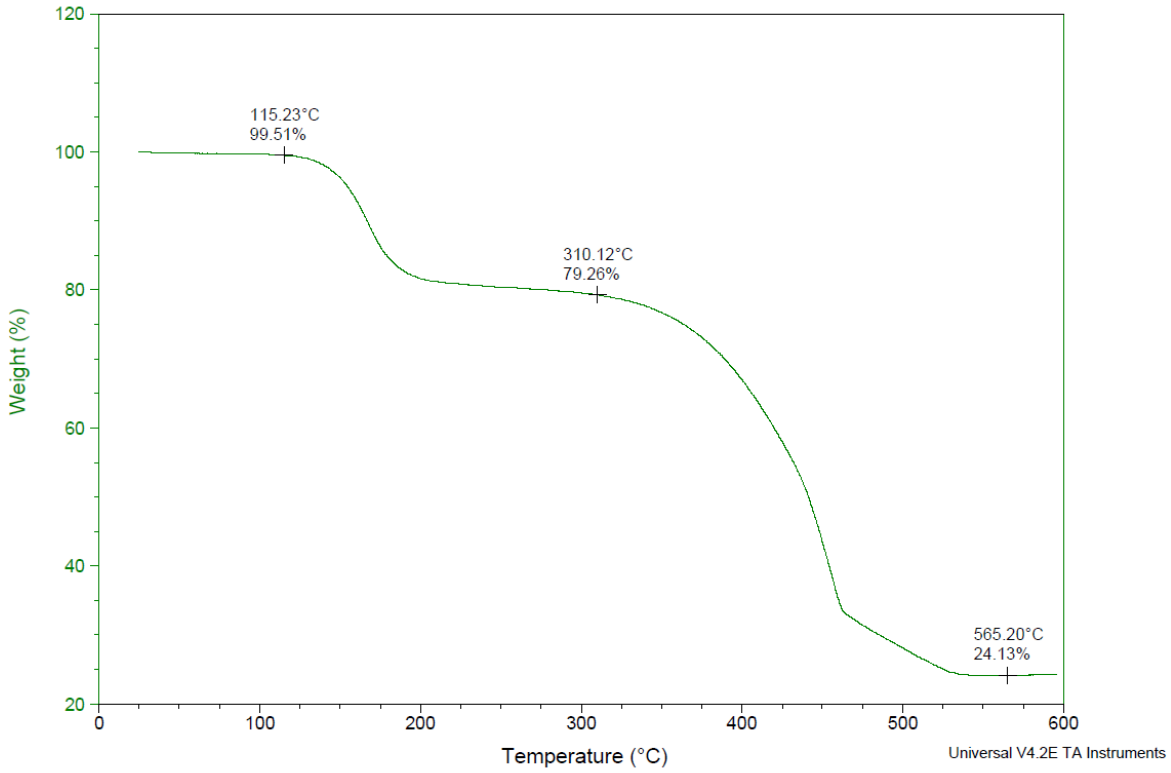

Figure S7: TGA of [4,4´-H_2bipy][$ZnCl_4$] (**3**). Size 3.769 mg Ramp 10.00 °C/min to 600.00 °C Balance Gas: Nitrogen 40.0 ml/min Sample Gas: Nitrogen 60.0 ml/min.

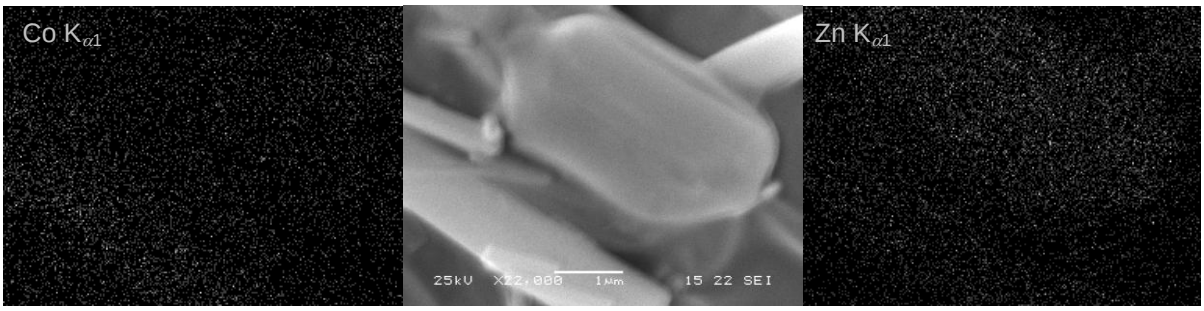

Figure S8: SEM images and Co $K_{\alpha 1}$ and Zn $K_{\alpha 1}$ EDAX map scans of $[\{(4,4'\text{-bipy})Co_{0.5}Zn_{0.5}Cl_2\}_n]$ (**$4_{0.5}$**) obtained by mixing 4,4′-bipy, $CoCl_2$ and $ZnCl_2$ in a 2:1:1 ratio in a solution of ethanol.

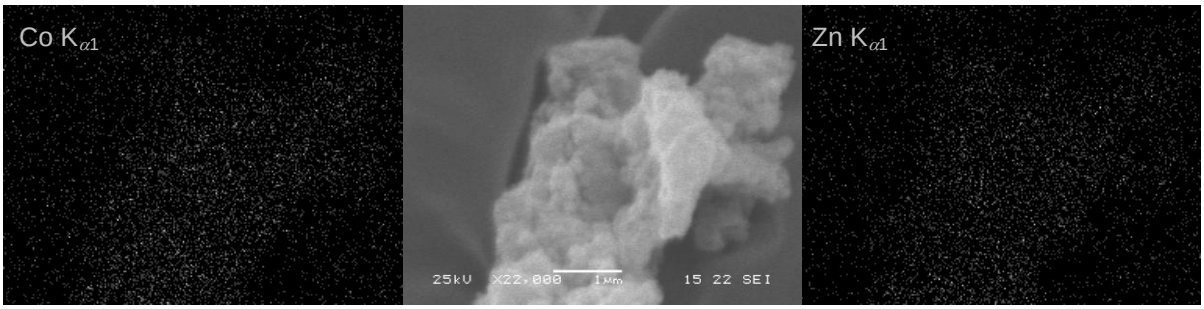

Figure S9: SEM images and Co $K_{\alpha 1}$ and Zn $K_{\alpha 1}$ EDAX map scans of $[\{(4,4'\text{-bipy})Co_{0.5}Zn_{0.5}Cl_2\}_n]$ (**$4_{0.5}$**) obtained by manually grinding 4,4′-bipy, $CoCl_2$ and $ZnCl_2$ in a 2:1:1 ratio with a drop of ethanol.

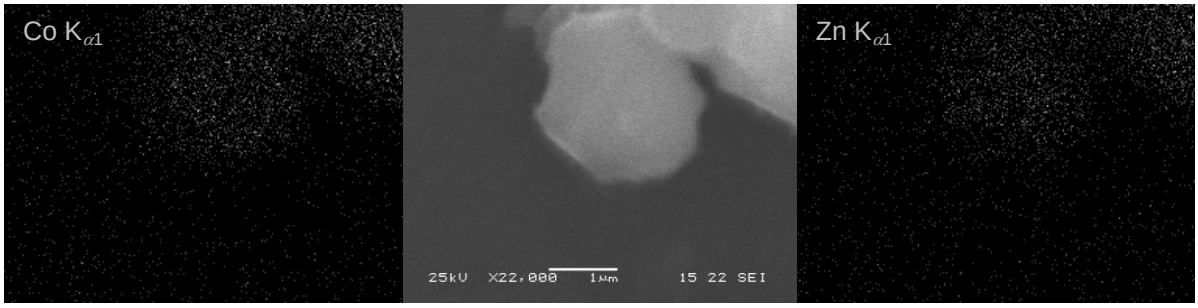

Figure S10: SEM images and Co $K_{\alpha 1}$ and Zn $K_{\alpha 1}$ EDAX map scans of $[4,4'\text{-}H_2bipy][Co_{0.5}Zn_{0.5}Cl_4]$ (**$3_{0.5}$**) obtained by grinding $[4,4'\text{-}H_2bipy]Cl_2$, $CoCl_2$ and $ZnCl_2$ in a 2:1:1 ratio.

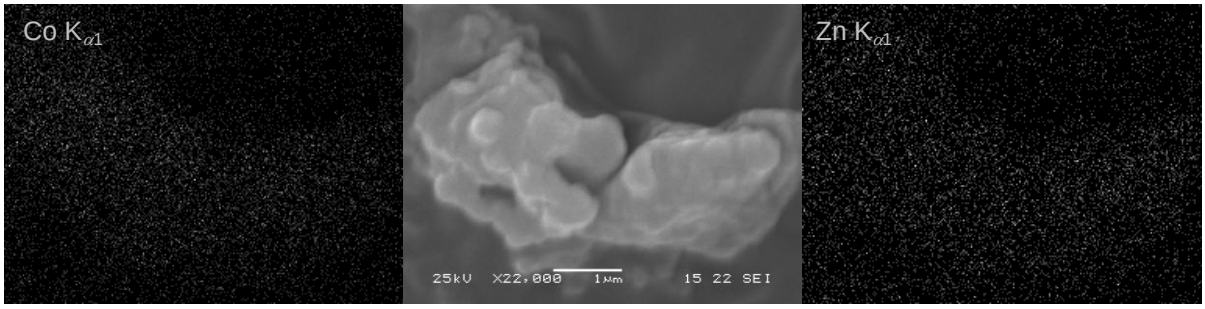

Figure S11: SEM images and Co $K_{\alpha 1}$ and Zn $K_{\alpha 1}$ EDAX map scans of $[\{(4,4'\text{-bipy})Co_{0.5}Zn_{0.5}Cl_2\}_n]$ (**$4_{0.5}$**) obtained by thermal elimination of 2 equivalents of HCl from $[4,4'\text{-}H_2bipy][Co_{0.5}Zn_{0.5}Cl_4]$ (**$3_{0.5}$**).

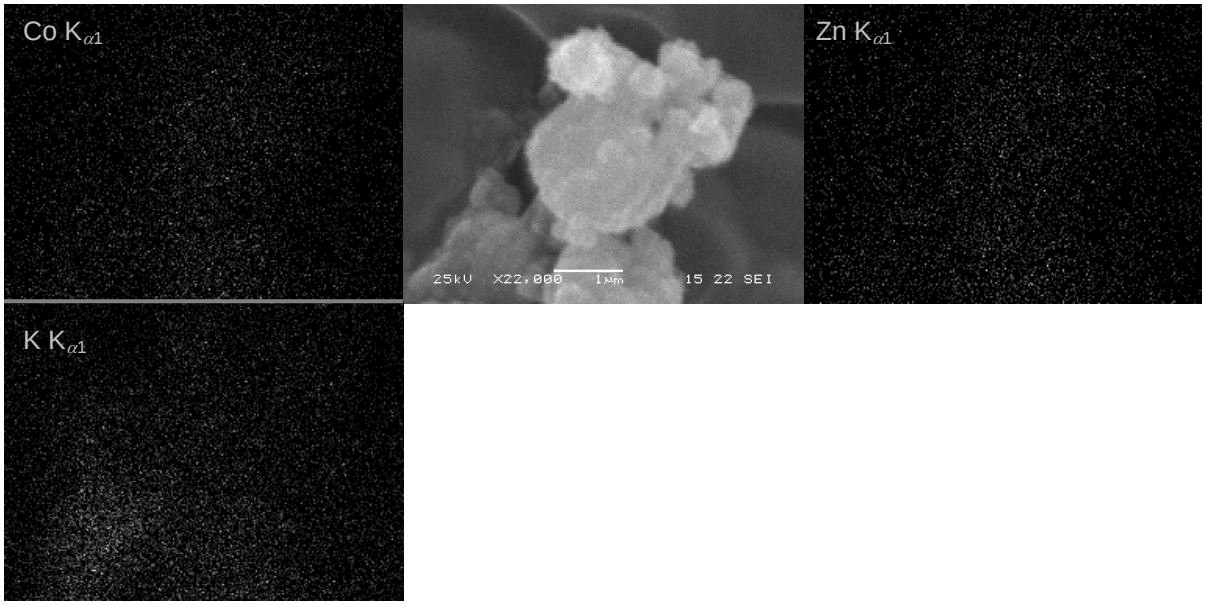

Figure S12: $K_{\alpha 1}$ and K $K_{\alpha 1}$ EDAX map scans of [{(4,4′-bipy)$Co_{0.5}Zn_{0.5}Cl_2$}$_n$] (**4$_{0.5}$**) obtained by mechanochemical elimination of 2 equivalents of HCl from from [4,4′-H_2bipy][$Co_{0.5}Zn_{0.5}Cl_4$] (**3$_{0.5}$**).

Compound reference	$\mathbf{3}_{0.86}$	$\mathbf{3}_{0.93}$	$\mathbf{3}_{0.95}$
Chemical formula	$C_{10}H_{10}Cl_4Co_{0.14}N_2Zn_{0.86}$	$C_{10}H_{10}Cl_4Co_{0.07}N_2Zn_{0.93}$	$C_{10}H_{10}Cl_4Co_{0.05}N_2Zn_{0.95}$
Formula Mass	364.48	364.90	364.90
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	7.6596(2)	7.65960(10)	7.6491(6)
b/Å	19.7497(7)	19.7388(4)	19.7209(16)
c/Å	9.4708(3)	9.4616(2)	9.4569(8)
α/°	90.00	90.00	90.00
β/°	109.067(2)	109.0620(10)	109.049(2)
γ/°	90.00	90.00	90.00
Unit cell volume/Å^3	1354.09(7)	1352.07(4)	1348.43(19)
Temperature/K	120(2)	120(2)	120(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
No. of formula units per unit cell, *Z*	4	4	4
Absorption coefficient, μ/mm^{-1}	2.504	2.544	2.473
No. of reflections measured	14086	17759	12415
No. of independent reflections	3096	3100	3745
R_{int}	0.0798	0.0334	0.0242
Final R_1 values ($I > 2\sigma(I)$)	0.0629	0.0216	0.0221
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1203	0.0489	0.0575
Final R_1 values (all data)	0.0915	0.0253	0.0228
Final $wR(F^2)$ values (all data)	0.1352	0.0503	0.0580
Goodness of fit on F^2	1.098	1.080	1.052

Table S1: Details of the crystal structure determinations of $\mathbf{3}_x$ with x = 0.95, 0.93 and 0.86