Variations to Spin Crossover in $[Fe_xZn_{(1-x)}(Me1,3bpp)_2(ClO_4)_2$ molecular alloys examined by Magnetometry and Single Crystal X-Ray Diffraction

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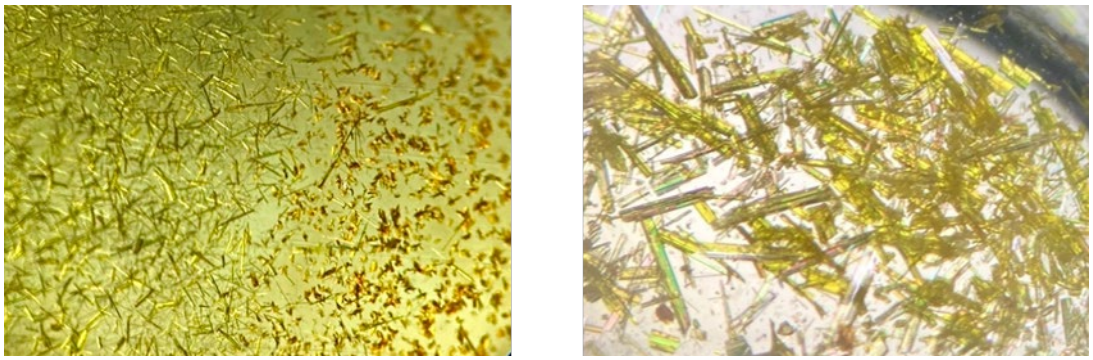

Figure S1. (Left) Non-homogenous (mixture of small yellow needles and light orange needles) crystalline samples from reactions of $Zn(ClO_4)_2$, $Fe(ClO_4)_2$ and Me-1,3bpp in amounts aiming at x>0.333 while using dry acetone as solvent. (Right) Homogenous crystalline sample of $[Fe_xZn_{1-x}(Me1,3bpp)_2](ClO_4)_2$ (**3*x***) obtained from the same reactions as above, in a mixture of dry acetone and ethanol (1:1 vol.).

Table S1. Analytical results from ICP-OES metal analysis for $[Zn(Me1,3bpp)_2](ClO_4)_2$ (**2**) and solid-solutions $[Fe_xZn_{1-x}(Me1,3bpp)_2](ClO_4)_2$ (**3*x***; x = 0.10, 0.15, 0.22, 0.33, 0.41, 0.48, 0.56, 0.64).

Empirical Formula	Fe/Zn stoichiometry used (expected weight %)	Expected av. MW [g/mol]	Metal content by ICP-OES [mass%]		Fe/Zn ratio by ICP-OES	Experimental av. MW [g/mol]
			Fe	Zn		
$Fe_{0.10}Zn_{0.90}C_{24}H_{22}N_{10}Cl_2O_8$	10/90 (0.78/8.24)	713.829	0.76	8.03	10/90	713.829
$Fe_{0.15}Zn_{0.85}C_{24}H_{22}N_{10}Cl_2O_8$	20/80 (1.57/7.34)	712.875	1.12	7.18	15.3/84.7	713.323
$Fe_{0.22}Zn_{0.78}C_{24}H_{22}N_{10}Cl_2O_8$	30/70 (2.35/6.43)	711.992	1.59	6.69	21.9/78.1	712.694
$Fe_{0.33}Zn_{0.67}C_{24}H_{22}N_{10}Cl_2O_8$	40/60 (3.14/5.52)	710.968	2.51	5.89	33.3/66.7	711.607
$Fe_{0.41}Zn_{0.59}C_{24}H_{22}N_{10}Cl_2O_8$	50/50 (3.93/4.6)	710.015	3.08	5.14	41.2/58.8	710.854
$Fe_{0.48}Zn_{0.52}C_{24}H_{22}N_{10}Cl_2O_8$	60/40 (4.73/3.69)	709.061	3.57	4.60	47.6/52.4	710.243
$Fe_{0.56}Zn_{0.44}C_{24}H_{22}N_{10}Cl_2O_8$	70/30 (5.52/2.77)	708.108	4.21	3.90	55.9/44.1	709.508
$Fe_{0.64}Zn_{0.36}C_{24}H_{22}N_{10}Cl_2O_8$	80/20 (6.32/1.85)	707.154	4.88	3.26	63.6/36.4	708.718

Table S2. C, N, H elemental analysis results for $[Zn(Me1,3bpp)_2](ClO_4)_2$ (**2**) and solid-solutions $[Fe_xZn_{1-x}(Me1,3bpp)_2](ClO_4)_2$ (**3*x***; x = 0.10, 0.15, 0.22, 0.33, 0.41, 0.48, 0.56, 0.64).

Best fit formula	Best fit composition	Element	Found (%)	Calculated (%)
$[Zn(Me1,3bpp)_2](ClO_4)_2 \cdot 0.37 H_2O$(7)	$ZnC_{24}H_{22.74}N_{10}Cl_2O_{8.37}$	C	40.63	39.96
		H	3.30	3.18
		N	18.74	19.41
$[Fe_{0.1}Zn_{0.9}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.69H_2O$	$Fe_{0.1}Zn_{0.9}C_{24}H_{23.38}N_{10}Cl_2O_{8.69}$	C	40.27	39.7
		H	3.16	3.24
		N	18.71	19.29
$[Fe_{0.153}Zn_{0.847}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.75H_2O$	$Fe_{0.153}Zn_{0.847}C_{24}H_{23.5}N_{10}Cl_2O_{8.75}$	C	40.39	39.66
		H	3.2	3.26
		N	18.54	19.27
$[Fe_{0.219}Zn_{0.781}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.69H_2O$	$Fe_{0.219}Zn_{0.781}C_{24}H_{23.38}N_{10}Cl_2O_{8.69}$	C	40.53	39.75
		H	3.19	3.25
		N	18.53	19.31
$[Fe_{0.333}Zn_{0.667}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.24H_2O$	$Fe_{0.333}Zn_{0.667}C_{24}H_{22.48}N_{10}Cl_2O_{8.24}$	C	40.51	40.27
		H	3.19	3.16
		N	19.32	19.56
$[Fe_{0.412}Zn_{0.558}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.35H_2O$	$Fe_{0.412}Zn_{0.558}C_{24}H_{22.7}N_{10}Cl_2O_{8.35}$	C	40.46	40.2
		H	3.15	3.19
		N	19.27	19.53
$[Fe_{0.476}Zn_{0.524}(Me\text{-}1,3bpp)_2](ClO_4)_2 \cdot 0.26H_2O$	$Fe_{0.476}Zn_{0.524}C_{24}H_{22.52}N_{10}Cl_2O_{8.26}$	C	40.51	40.32
		H	3.14	3.18
		N	19.4	19.59
$[Fe_{0.559}Zn_{0.441}Me1,3bpp)_2](ClO_4)_2 \cdot 0.58H_2O$	$Fe_{0.559}Zn_{0.441}C_{24}H_{23.16}N_{10}Cl_2O_{8.58}$	C	40.35	40.04
		H	3.16	3.24
		N	19.14	19.45
$[Fe_{0.636}Zn_{0.364}(Me1,3bpp)_2](ClO_4)_2 \cdot 0.21H_2O$	$Fe_{0.636}Zn_{0.364}C_{24}H_{22.42}N_{10}Cl_2O_{8.21}$	C	40.74	40.46
		H	3.13	3.17
		N	19.38	19.66

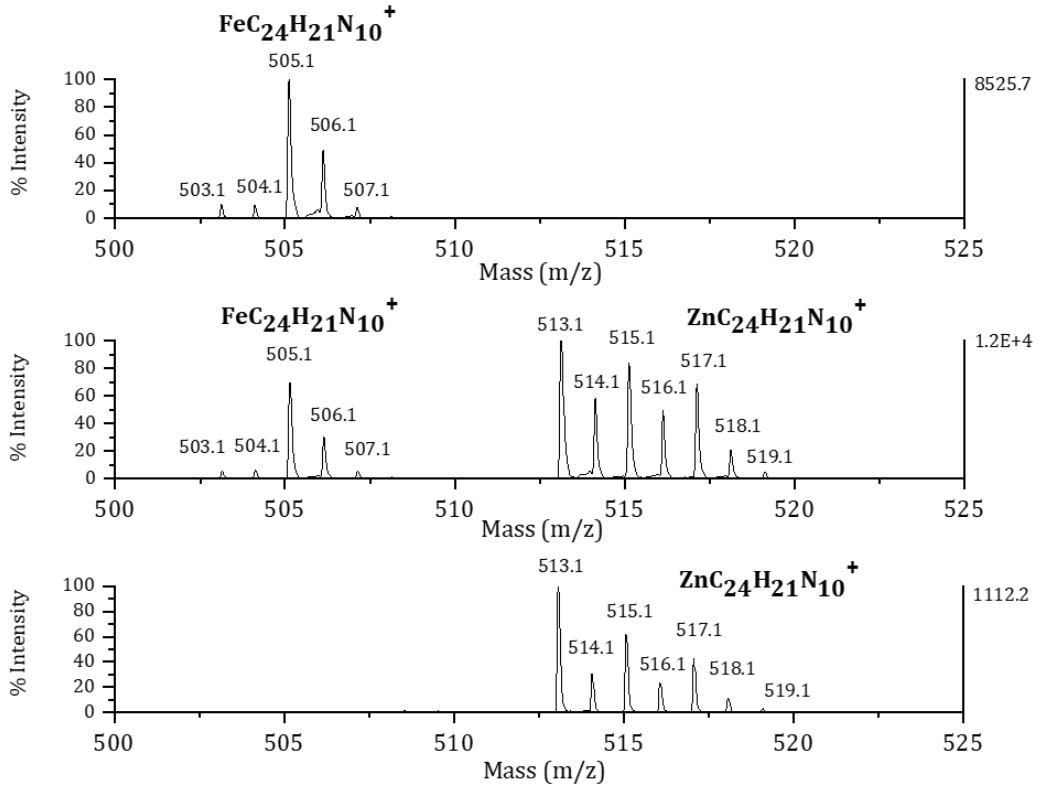

Figure S2. Selected region of the positive-ion MALDI mass spectrograms for $[Fe(Me1,3bpp)_2](ClO_4)_2$ (**1**, top), $[Fe_xZn_{1-x}(Me1,3bpp)_2](ClO_4)_2$ (**3*x***; x = 0.2, middle) and $[Zn(Me1,3bpp)_2](ClO_4)_2$ (**2**, bottom). The corresponding peaks at 505.1 and 513.1 exhibited by **3*x*** (x = 0.2) corroborate the presence of both complexes (that of **1** and **2**, respectively) in the solid solution.

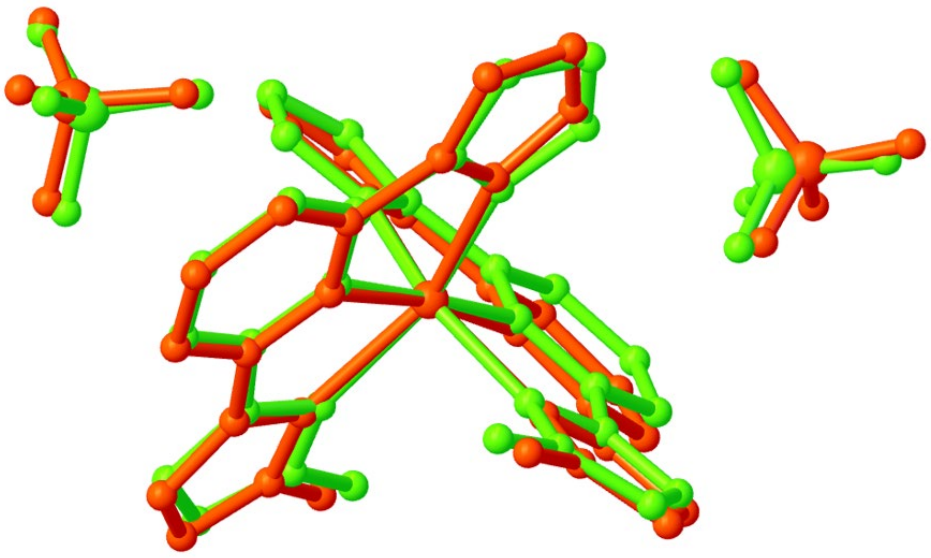

Figure S3. Overplayed crystal structures of reported $[Fe(Me1,3bpp)_2](ClO_4)_2$ (**1**, orange) and $[Zn(Me1,3bpp)_2](ClO_4)_2$ (**2**, green) at 100K.

Table S3. Crystallographic data, average Fe-N bond lengths and distortion parameters for $[Zn(Me1,3bpp)_2](ClO_4)_2$ (**2**) and (for comparison) $[Fe(Me\text{-}1,3bpp)_2](ClO_4)_2$ (**1**).

Compound	**1**	**2**
Formula	$C_{24}H_{22}Cl_2FeN_{10}O_8$	$C_{24}H_{22}Cl_2ZnN_{10}O_8$
FW (g mol^{-1})	705.26	714.78
T(K)	100	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	*C*2/c	
a (Å)	41.290(9)	41.768(3)
b (Å)	8.0448(15)	8.1368(5)
c (Å)	17.843(4)	17.9388(11)
β (°)	108.946(14)	112.214(3)
V (Å^3)	5606(2)	5644.2(6)
Z	8	8
ϱ_{calcd} (g cm^{-3})	1.671	1.682
μ (mm–1)	0.798	1.128
Independent reflections (R_{int})	3428(0.2227)	6498 (0.0411)
Restrains/parameters	82 / 415	0/ 416
Goodness-of-fit on F^2	1.059	1.036
Final R_1 /wR_2 [$I>2\sigma(I)$]	0.0700 / 0.1355	0.0361/ 0.0801
Final R_1 /wR_2 [all data]	0.1200 / 0.1553	0.0491 / 0.0855
Largest diff. peak and hole (e Å^3)	0.881 / –0.412	0.609 / -0.551
<Fe–N>	1.96(4)	2.16(1)
Σ	93.3(1)	137.1(3)
Θ	367.8	445.7(6)

Table S4. Distances of selected π···π and C-H··· π interactions within compounds **1** and **2** at 100k.

interaction	Labels	Distance (Å) to centroid	Compd.
π···π (1)	Cg(N1N2C2C3C4)···Cg(N4N5C10C11C12)	3.566	**1**
C−H···π (1)	C1−H1B···Cg(N9N10C22C23C24)	3.272	**1**
C−H···π (2)	C12−H12···Cg(N6N7C14C15C16)	2.584	**1**
C−H···π (2)	C24−H24···Cg(N4N5C10C11C12)	3.320	**1**
C−H···π (2)	C24−H24···Cg(N6N7C14C15C16)	4.219	**1**
C−H···π (2)	C15−H15···Cg(N1N2C2C3C4)	3.154	**1**
C−H···π (2)	C15−H15···Cg(N9N10C22C23C24)	3.070	**1**
π···π (1)	Cg(N1N2C2C3C4)···Cg(N4N5C10C11C12)	3.474	**2**
C−H···π (1)	C1−H1B···Cg(N9N10C22C23C24)	3.145	**2**
C−H···π (2)	C12−H12···Cg(N6N7C14C15C16)	2.756	**2**
C−H···π (2)	C24−H24···Cg(N4N5C10C11C12)	3.548	**2**
C−H···π (2)	C24−H24···Cg(N6N7C14C15C16)	4.164	**2**
C−H···π (2)	C15−H15···Cg(N1N2C2C3C4)	3.550	**2**
C−H···π (2)	C15−H15···Cg(N9N10C22C23C24)	2.972	**2**

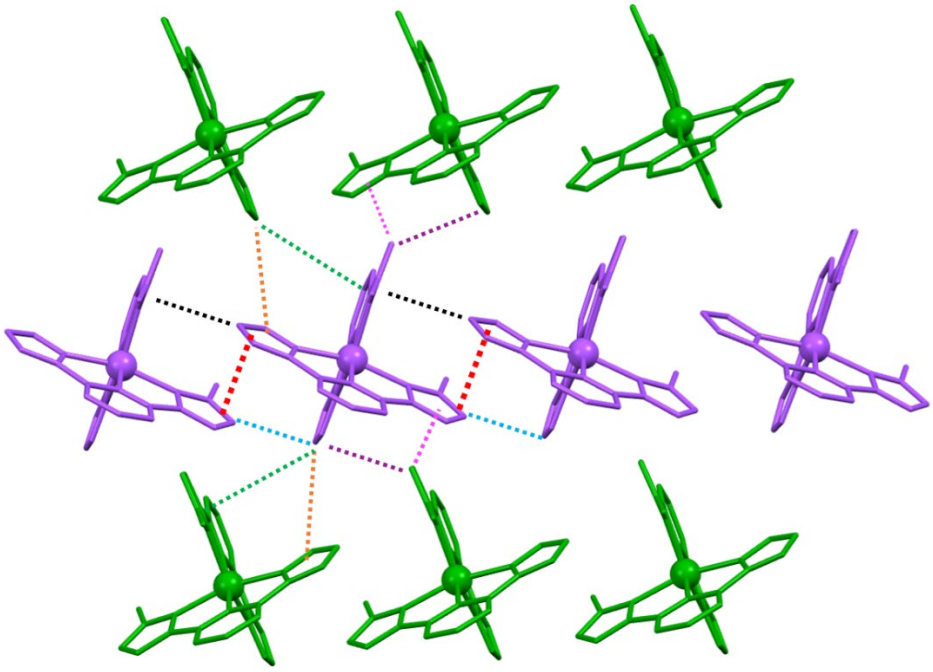

Figure S4. Sheet organization of the cations of **2**, emphasizing the intermolecular interactions formed by each complex with its first-neighbors (shown in colors for reference in Table S4). The two different orientations of the cations are shown in green and purple.

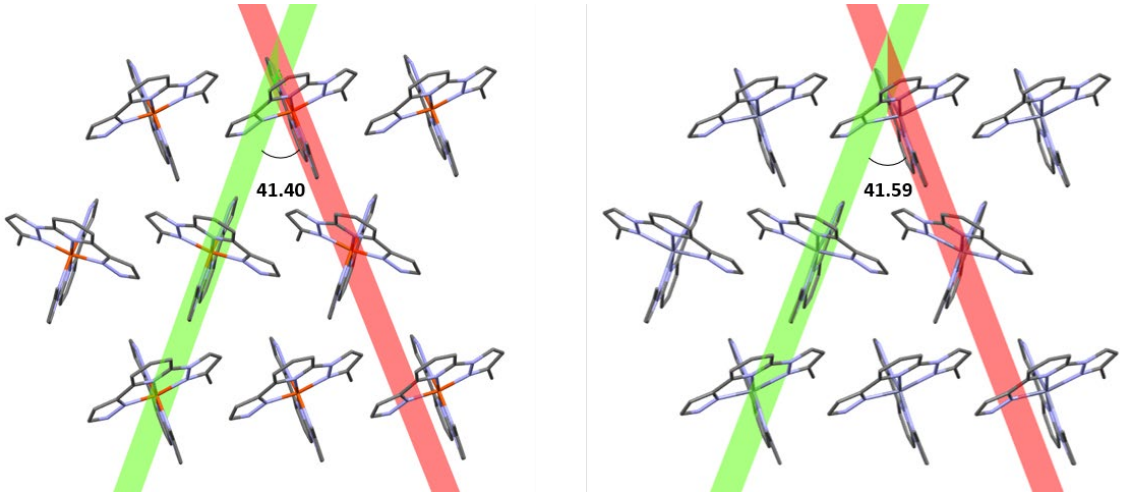

Figure S5. Angle between complexes in the two different orientations for $[Fe(Me\text{-}1,3bpp)_2](ClO_4)_2$ (**1**, left) and $[Fe(Me\text{-}1,3bpp)_2](ClO_4)_2$ (**2**, right), measured using idealized planes of two equivalent ligands.

Table S5. Crystallographic data, average Fe-N bond lengths and distortion parameters for $[Fe_xZn1\text{-}_x(Me1,3bpp)_2](ClO_4)_2$ (**3x**). Anisotropic data.

x	**x:0.10**	**x:0.15**	**x:0.22**	**x:0.33**	**x:0.41**	**x:0.48**	**x:0.56**	**x:0.64**
Formula	C24 H22 Fe0.164 N10 Zn0.836, 2(ClO4)	C24 H22 Fe0.19 N10 Zn0.81, 2(ClO4)	C24 H22 Fe0.166 N10 Zn0.834, 2(ClO4)	C24 H22 Fe0.381 N10 Zn0.619, 2(ClO4)	C24 H22 Fe0.498 N10 Zn0.502, 2(ClO4)	C24 H22 Fe0.618 N10 Zn0.382, 2(ClO4)	C24 H22 Fe0.664 N10 Zn0.336, 2(ClO4)	C24 H22 Fe0.655 N10 Zn0.345, 2(ClO4)
FW (g mol^{-1})	713.21	712.96	713.20	711.16	710.05	708.89	708.47	708.55
T(K)	100K							
Wavelength (Å)	0.71073							
Crystal system	monoclinic							
Space group	C 2/c							
a (Å)	41.8400(14)	41.7962(11)	41.853(5)	41.717(3)	41.6935(17)	41.601(2)	41.5382(14)	41.5818(15)
b (Å)	8.1139(3)	8.1127(2)	8.1030(10)	8.0829(8)	8.0820(4)	8.0751(5)	8.0675(3)	8.0616(3)
c (Å)	17.9721(6)	17.9490(5)	17.949(2)	17.9611(15)	17.9300(8)	17.9077(10)	17.8837(6)	17.9002(6)
β (°)	112.037(2)	112.017(2)	112.073(5)	111.545(5)	111.141(3)	110.962(3)	110.542(2)	110.605(2)
V ($Å^3$)	5655.5(3)	5642.3(3)	5640.8(12)	5633.2(9)	5635.2(5)	5617.7(6)	5611.9(3)	5616.6(4)
Z	8							
ρ_{calcd} (g cm^{-3})	1.675	1.679	1.680	1.677	1.674	1.676	1.677	1.676
μ (mm−1)	1.071	1.065	1.073	1.002	0.963	0.925	0.911	0.913
Independent reflections (R_{int})	6465 (0.0455)	8360(0.0542)	5231(0.0545)	5743(0.0845)	5742 (0.0636)	6881(0.0618)	5982(0.0495)	7562(0.0463)
Restrains/parameters	14/419	28/433	14/ 419	14/ 419	14/ 419	14/ 420	14/ 419	28/ 429
Goodness-of-fit on F^2	1.024	1.025	1.022	1.046	1.049	1.037	1.039	1.047
Final R_1 /wR_2 [I>2σ(I)]	0.0385/0.0813	0.0421/ 0.0890	0.0391/ 0.0843	0.0499/ 0.0980	0.0489/ 0.0969	0.0485/ 0.1110	0.0441/ 0.1000	0.0429/ 0.0891
Final R_1 /wR_2 [all data]	0.0593/0.0914	0.0675/0.0991	0.0581/ 0.0925	0.0922/ 0.1144	0.0969/ 0.1097	0.0758/ 0.1240	0.0613/ 0.1078	0.0648/ 0.0972
Largest diff. peak and hole (e $Å^3$)	0.584/ -0.515	0.400/-0.542	0.318/ -0.350	0.354/ -0.507	0.623/ -0.511	0.486/ -0.650	0.478/ -0.604	0.392/ -0.432
<Fe–N>	2.155	2.155	2.156	2.127	2.104	2.089	2.066	2.070
Σ	136.9(3)	136.8(2)	137.8(3)	131.6(4)	126.6(4)	123.4(3)	117.3(3)	119.3(3)
Θ	444.5(7)	444.1(6)	447.3(8)	425.7(10)	409.7(9)	399.5(8)	378.6(8)	385.0(7)

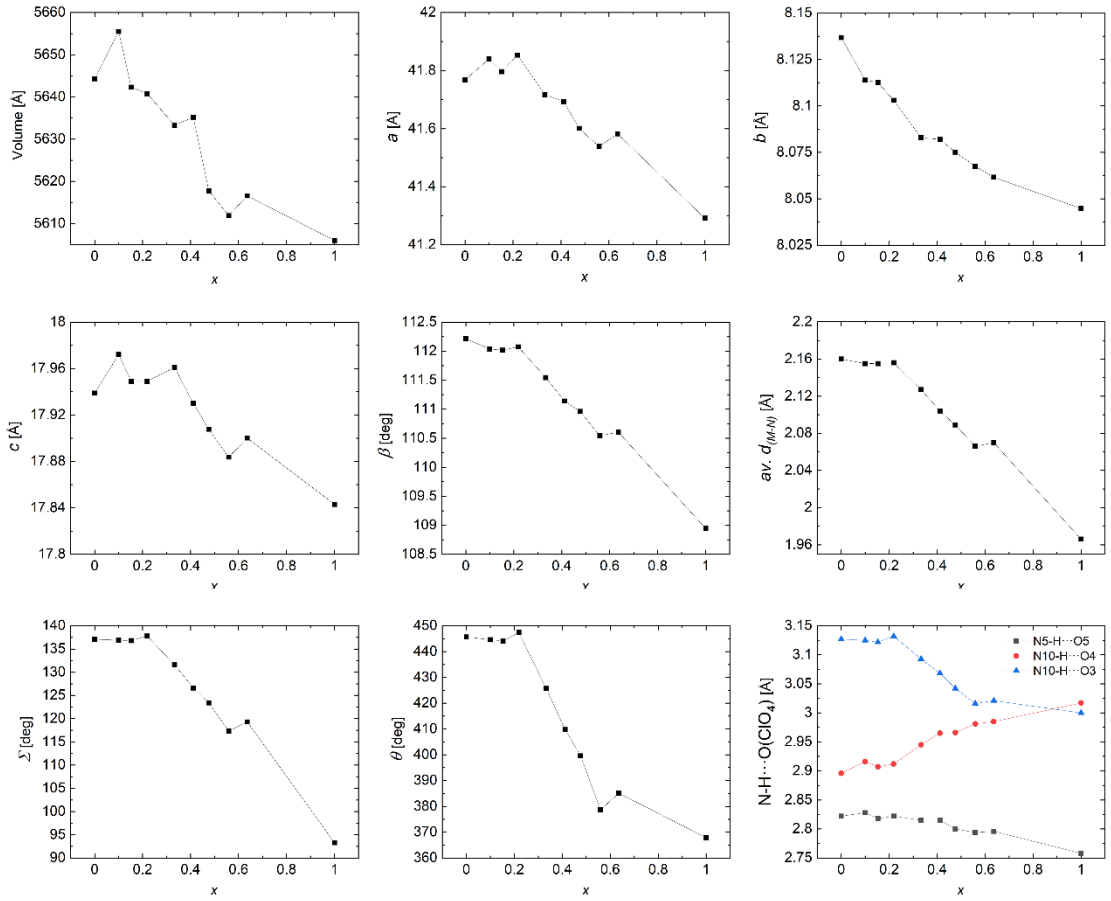

Figure S6. Plots of (from left to right and top to bottom) unit cell volume, unit cell parameters *a*, *b*, *c* and *β*, average M−N bond distances (M= Fe/Zn position), distortion parameters Σ and θ and N−H···O hydrogen bond distances to perchlorates *versus* *x* for the solid solutions $[Fe_xZn_{1-x}(Me1,3bpp)_2](ClO_4)_2$ (**3*x***) and compounds **1** and **2**. The systematic anomaly for x = 0.636 coincides with the fact that this data set was refined differently because of the presence of disorder on the ClO_4^- anions.

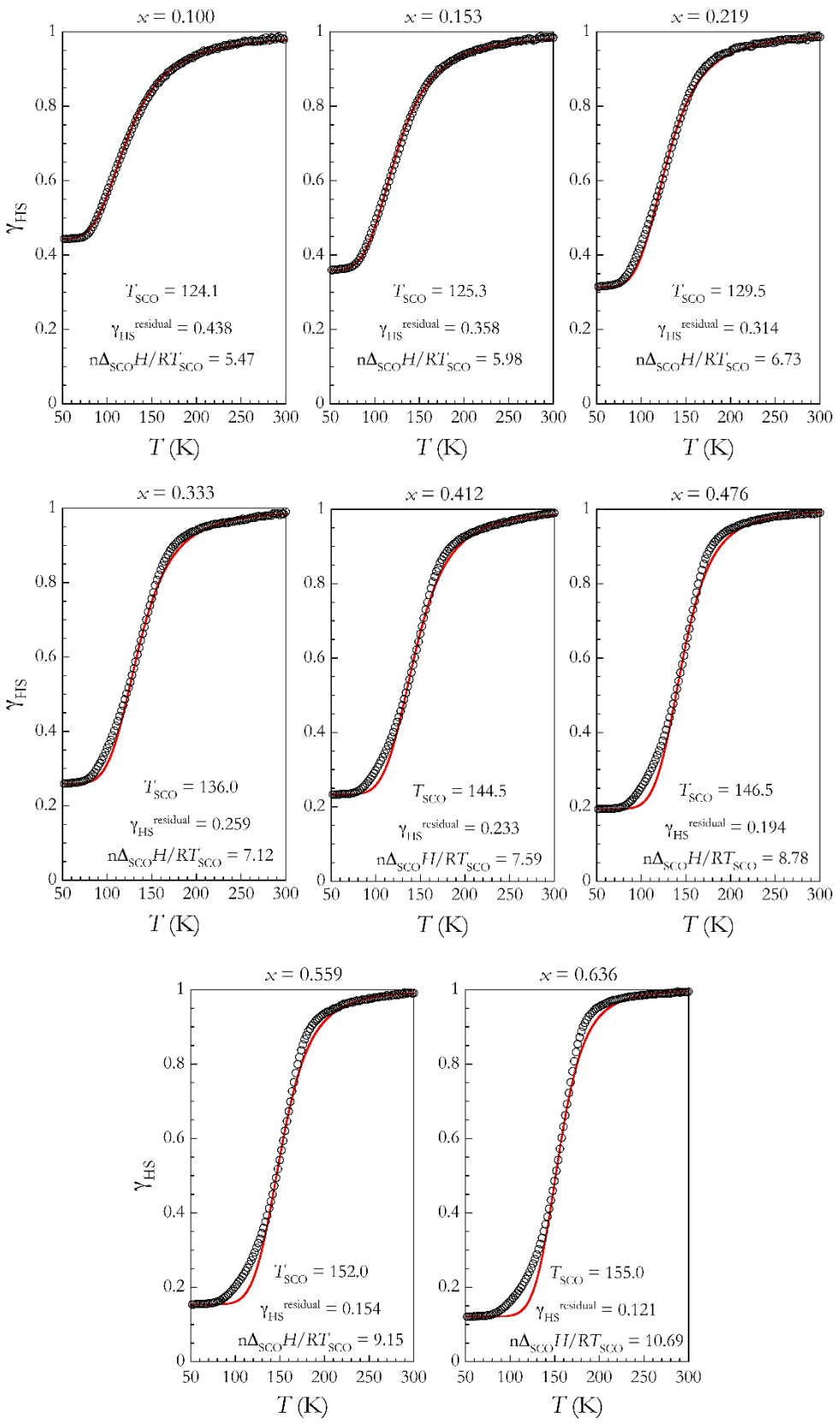

Figure S7. Temperature dependence of the HS fraction γ_{HS} in compounds **3*x*** and fits of Eq. 1 (see main text) to these (full red lines) for the given value of T_{SCO}, $\gamma_{HS}^{residual}$ and $n\Delta_{SCO}H/RT_{SCO}$.