Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information (ESI) for:

Post-synthetic Anion Exchange in Iron(II) 1,2,4-Triazole Based Spin Crossover Materials via Mechanochemistry

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SQUID Magnetometry

Multiple thermal cycles for all compounds presented are given in Figures S1 - S5. In all compounds, the SCO observed in the initial heating cycle occurs at higher temperature than during subsequent thermal cycles. This is attributed here to the loss of water from the complexes at high temperature, as shown in the thermogravimetric analysis data presented below. Such differences in the first thermal cycle are not uncommon for this class of material, as discussed in the main manuscript text.

Compound 1

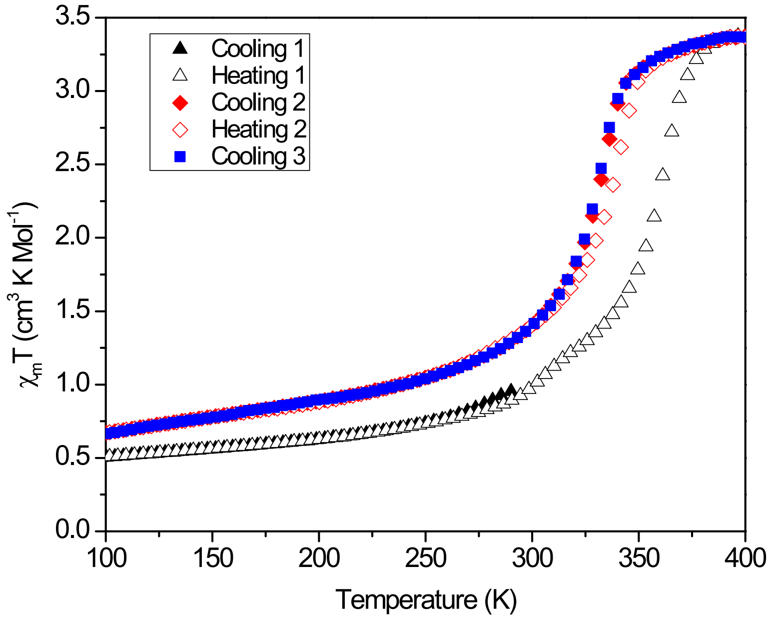

Figure S 1: Multiple cycles Squid data for compound **1**. □ Cycle 1 Cool, ❐ Cycle 1 Heat, ◆ Cycle 2 Cool, ◊ Cycle 2 Heat and ■Cycle 3 Cool.

Compound 1-Cl

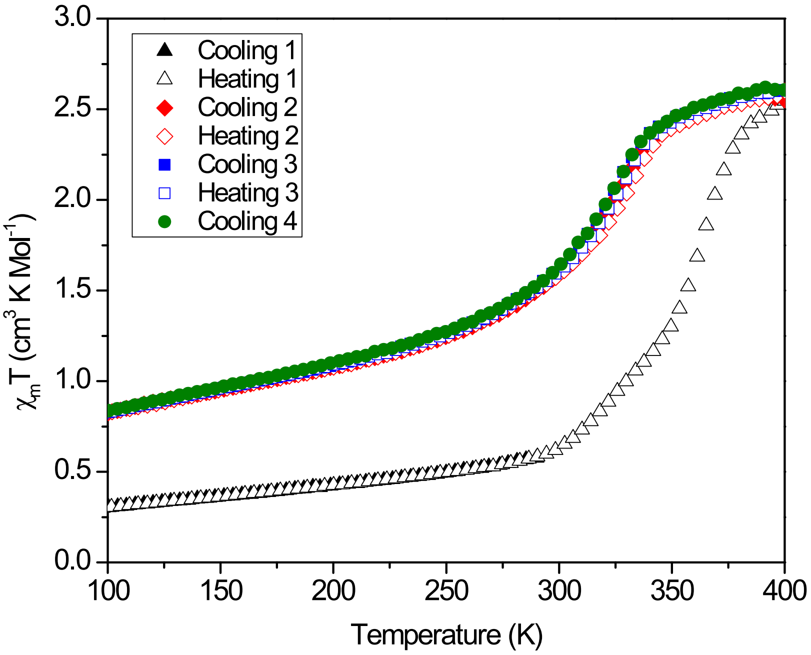

Figure S 2: Multiple cycles Squid data for compound **1-Cl**. ☐ Cycle 1 Cool, ❒ Cycle 1 Heat, ◆ Cycle 2 Cool, ◊ Cycle 2 Heat, ■Cycle 3 Cool, ☐ Cycle 3 Heat and ● Cycle 4 Cool.

Compound 1-F

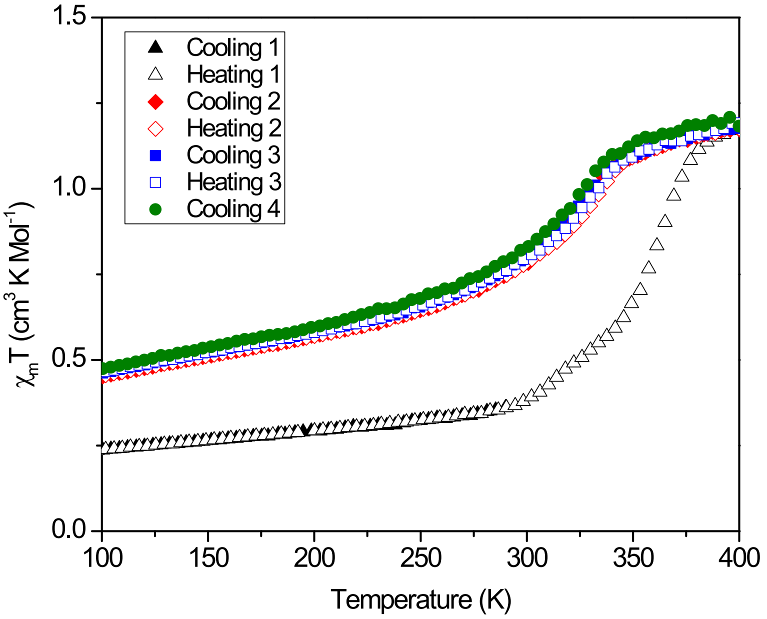

Figure S 3: Multiple cycles Squid data for compound **1-F**. ☐ Cycle 1 Cool, ❒ Cycle 1 Heat, ◆ Cycle 2 Cool, ◊ Cycle 2 Heat, ■Cycle 3 Cool, ☐ Cycle 3 Heat and ● Cycle 4 Cool.

Compound 1-Br

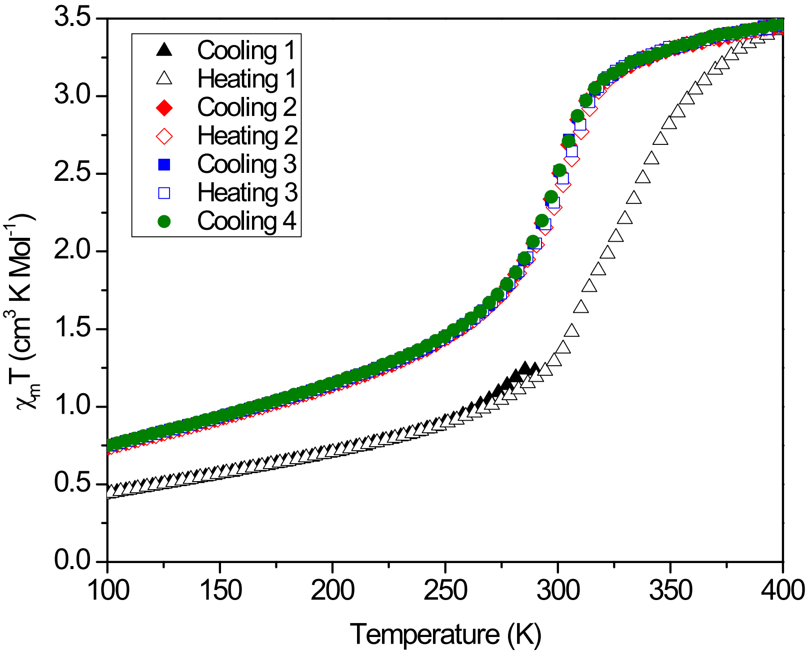

Figure S 4: Multiple cycles Squid data for compound **1-Br**. □ Cycle 1 Cool, ❐ Cycle 1 Heat, ◆ Cycle 2 Cool, ◊ Cycle 2 Heat, ■Cycle 3 Cool, □ Cycle 3 Heat and ● Cycle 4 Cool.

Compound 1-I

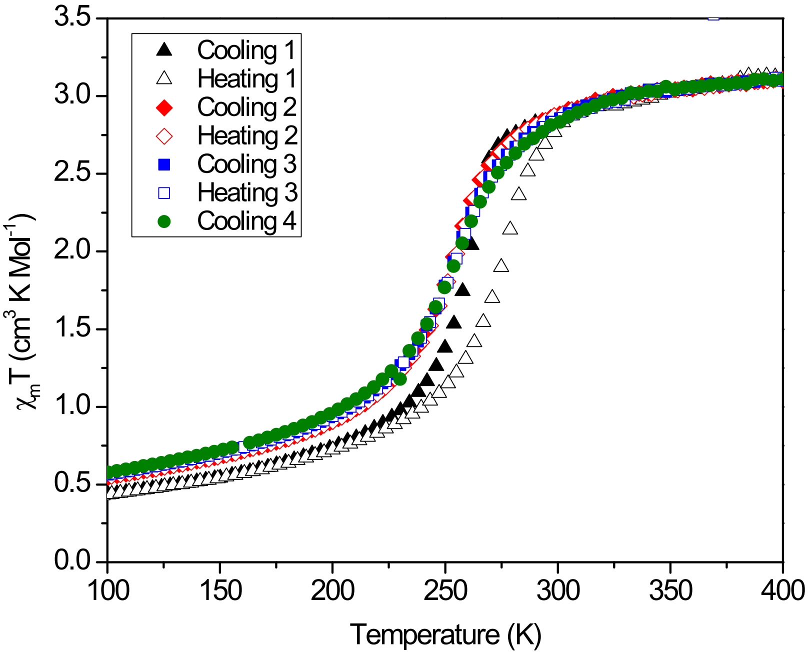

Figure S 5: Multiple cycles Squid data for compound **1-I**. □ Cycle 1 Cool, ❐ Cycle 1 Heat, ◆ Cycle 2 Cool, ◊ Cycle 2 Heat, ■Cycle 3 Cool, □ Cycle 3 Heat and ● Cycle 4 Cool.

Powder diffraction

Additional experimental details

Scherrer analysis of compound **1** and compound **1-Cl**, was carried out using PXRD data collected on a Panalytical X'Pert3 using Cu Kα radiation, λ = 1.54051 Å, with a power rating 40 kV and 20 mA. The 2θ range 5 – 40° was recorded with continuous scanning using a step size of 0.0041778° with 400 seconds exposure per step. Samples were mounted on a silicon crystal sample holder. A LaB_6 standard was used to determine instrumental peak broadening.

Comments on the use of the Scherrer Equation

Due to the number of assumptions made in the application of the Scherrer equation, the change in coherent domain size resulting from the SSM procedure is more significant than the absolute particle size. The Scherrer equation includes a dimensionless shape factor which accounts for the shape of the crystallite, the value used in calculations assumes a spherical particle shape. Triazole SCO materials have previously been shown to have different shapes depending on the method of synthesis, including spheres, rods and plates.[1]

1 L. Salmon and L. Catala, *Comptes Rendus Chim.*, 2018, **21**, 1230–1269.

TEM

Additional experimental details

TEM was performed using a Jeol 1230 120 kV transmission electron microscope equipped with a Gatan One View 16mp camera with automatic drift correction. Due to significant aggregation of the particles, samples were prepared by adapting the method described by Petri-Fink *et al.*[33] 10 mg of the sample was added to MilliQ water (10 mL) and sonicated for 30 minutes. Bovine serum albumin (BSA) (15 mg) was dissolved in MilliQ water (10 mL) and sonicated for 15 minutes. An aliquot of the BSA solution (100 µL) was added to an aliquot of the compound solution (100 µL) and sonicated for an additional 15 minutes. 600 Mesh coppers grids purchased from Agar Scientific were coated in ~70 nm of formvar and ~5 nm of evaporated carbon using a QuorumQ150T ES Evaporative coater. 2 µL aliquots of sample/BSA solution were deposited on the copper grids and vacuum dried at 30 °C for 30 minutes.

Compound 1

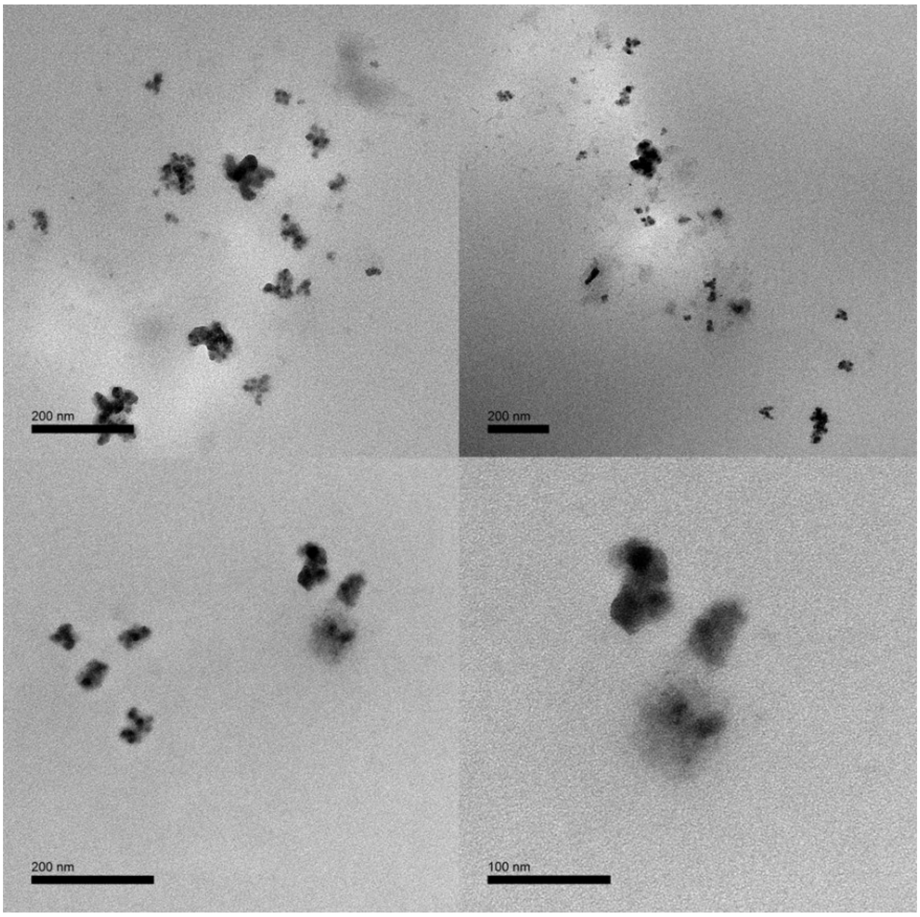

Figure S 6: Additional TEM images for compound **1**.

Compound 1-Cl

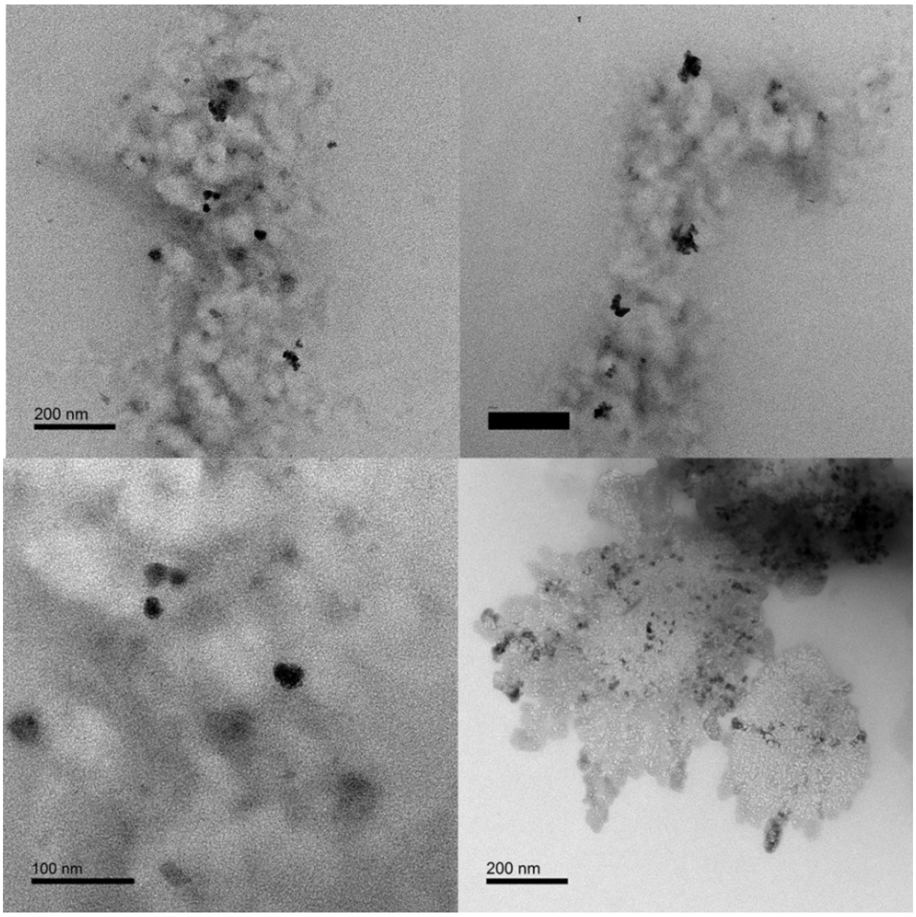

Figure S 7: Additional TEM images for compound **1-Cl**.

EDX

Additional experimental details

EDX measurements were recorded using a Hitachi-3400n SEM fitted with an Oxford Instruments X-Max 80mm^2 SDD. The data were recorded in the 0-20 KeV range with 20 s live time and 5 s processing time. The samples were analysed as rough particles without polishing, and consequently the potential error within the reported values for elemental composition is not insignificant. This is evident in the values obtained for standard deviation of the absolute elemental composition in the samples. As such, the relative ratios of elements are more instructive than absolute values. Table S1 shows the average % weight of elements per sample based on EDX measurements.

Table S1: Average % weight of elements per sample based on EDX measurements. *The elemental composition of the **1-F** sample was strongly location dependent with significant variation in the presence of NaF. This is due to the relative insolubility of NaF in alcohol preventing sufficient washing.[2]

Sample	**C %**	**N %**	**Na %**	**Fe %**	**Cl %**	**Br %**	**I%**	**F%**
1-Cl	23.24 ± 1.15	42.99 ± 6.53	0.36 ± 0.10	12.41 ± 3.63	16.70 ± 4.85	-	-	-
1-F	17.83 ± 0.30	29.69 ± 0.48	6.68 ± 1.22	13.41 ± 2.88	11.62 ± 1.02	-	-	**16.11 ± 3.05**
[Fe(atrz)$_3$]Cl$_2$	19.00	44.35	-	14.74	18.71	-	-	-
1-Br	20.60 ± 1.32	37.09 ± 4.25	0.50 ± 0.10	8.38 ± 1.71	1.22 ± 0.29	27.52 ± 4.74	-	-
[Fe(atrz)$_3$]Br$_2$	15.39	35.92	-	11.94	-	34.16	-	-
1-I	18.42 ± 0.65	40.34 ± 3.46	-	6.22 ± 0.78	0.59 ± 0.05	-	30.21 ± 4.10	-
[Fe(atrz)$_3$]I$_2$	12.82	29.91	-	9.94	-	-	45.18	-

[2] V. A. Stenger, *J. Chem. Eng. Data*, 1996, **41**, 1111–1113.

IR Spectroscopy

IR spectra for all samples reported are shown in Figure S8.

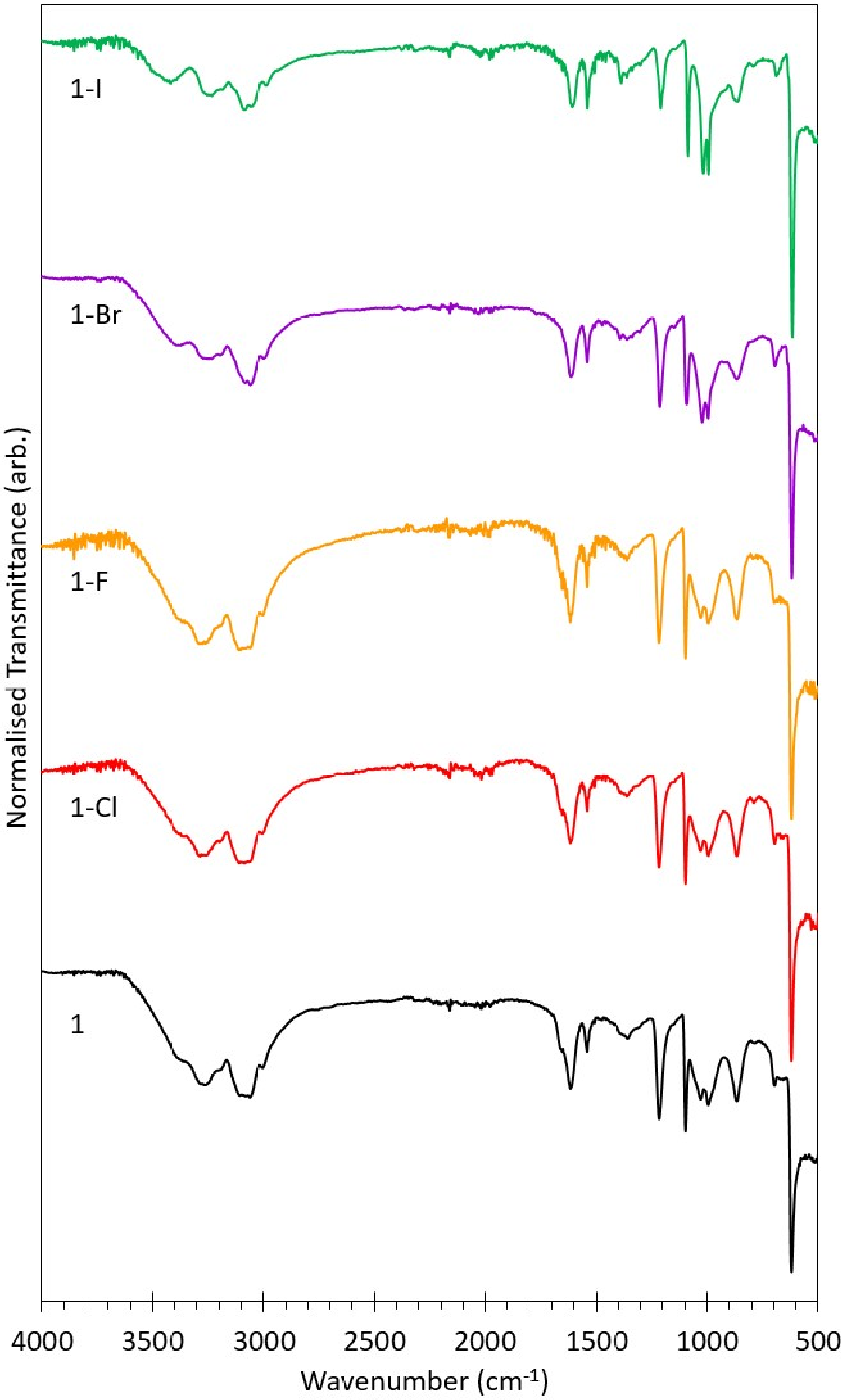

Figure S 8: Normalised IR spectra for all samples

Thermogravimetric analysis

Thermogravimetric analysis of all compounds is presented in Figure S9. Assuming all water is removed by 150°C, the calculated number of water molecules, n, per formula unit for each complex is shown in Table S2.

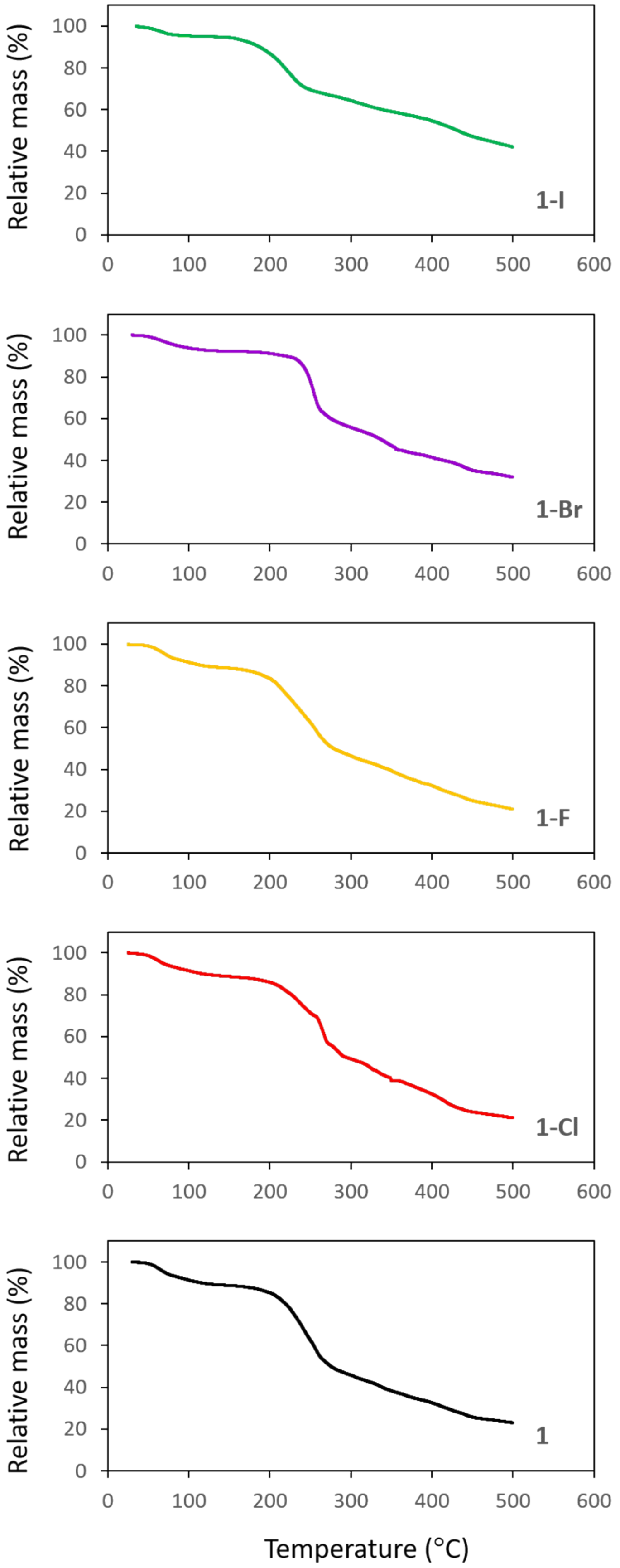

Figure S9. Thermogravimetric analysis for all compounds.

Table S2. Number of water molecules, n, per formula unit $Fe(atrz)_3A_2 \cdot nH_2O$, where A = Cl, Br or I as appropriate calculated from TGA measurements in Figure S9.

Sample	n
1	2.66
1-Cl	2.67
1-F	2.74
1-Br	2.16
1-I	1.82