Electronic Supplementary Material (ESI) for Dalton Transactions.

Spin Crossover {[Fe(atrz)$_3$](OTs)$_2$}$_n$ Monolith: A green Synthesis Approach for Robust Switchable Materials

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1) Experimental Section

Materials. Chemicals and reagents were purchased from commercial suppliers and used as received.

Physical measurements.

- TGA was performed using a TA Instrument TGAQ500 with a ramp of 2 K min^{-1} under air from 303 K to 873 K.
- FTIR spectra were recorded as neat samples in the range 400-4000 cm^{-1} on a Bruker Tensor 27 (ATR device) Spectrometer.
- Elemental analyses (C, H and N) were performed on a LECO CHNS-932 Analyzer at the "Servicio Interdepartamental de Investigación (SIdI)" at Autónoma University of Madrid.
- Magnetic susceptibility measurements were carried out in a Quantum Design MPMS-5S SQUID magnetometer under a 10000 Oe field at a rate of 2 K·min^{-1}. Each sample was secured inside a plastic capsule. Pascal constants were used to correct for the diamagnetic contribution.
- Dynamic light scattering (DLS) was carried out in a Malvern Zetasizer Nano-ZS in tetrahydrofuran (THF) at room temperature, with quartz glass cuvettes.
- Scanning Electron Microscopy (SEM) images were obtained in a field emission (FE-SEM), SIGMA 360 VP Carl Zeiss equipment, at 2kV.

2) Synthesis of 1, 2 and 3

Compound **1** was synthesized at room temperature, by adding drop by drop a solution of 0.59 mmol of atrz (atrz = 4-Amino-4H-1,2,4-triazole) in 3 mL of ethanol on top of a solution of 0.20 mmol of $[Fe(H_2O)_6](OTs)_2$ (OTs = *p*-tolouenesulfonate) in 3 mL of distilled water. The solution was stirred for 1 h, filtered, and washed with ethanol. Compound **1** was obtained as a pink powder in 87% yield.
Anal. calcd for **1** $0.4H_2O$: C 36.53%, H 4.11%, N 25.56%; found C 36.34%, H 4.05%, N 25.79%.

Compound **2** was synthesized at room temperature by adding a solution of 3 mmol of atrz in 5 mL of ethanol on top of a solution of 1 mmol of $[Fe(H_2O)_6](OTs)_2$ in 5 mL of ethanol. The solution was stirred for 30 minutes, filtered, and washed with ethanol. Compound **2** was obtained as a pink powder in 79% yield.
Anal. calcd for **2** $0.4H_2O$: C 36.53%, H 4.11%, N 25.56%; found C 36.59%, H 4.05%, N 25.83%.

Compound **3** was synthesized at room temperature by adding a solution of 3 mmol of atrz in 5 mL of ethanol on top of a solution of 1 mmol of $[Fe(H_2O)_6](OTs)_2$ in 5 mL of ethanol. The solution was stirred for 30 minutes, centrifuged (5000 rpm, 15 minutes, RT), and washed with 10 mL of ethanol three times. Compound **3** was obtained as a purple dense and compact monolith in 83% yield.
Anal. calcd for **3** $0.65H_2O$: C 36.28%, H 4.16%, N 25.38%; found C 36.36%, H 4.36%, N 25.56%.

3) Fourier Transform Infrared Spectroscopy (FTIR)

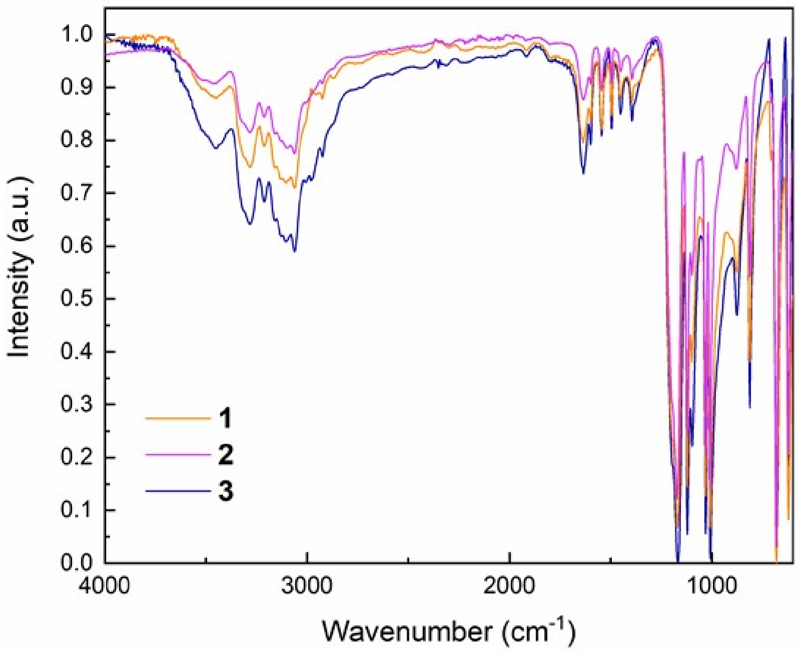

Figure S1. FTIR spectra of **1**, **2** and **3** between 4000 and 600 cm^{-1}.

FTIR **1** (cm^{-1}): ν = 3441 (w; ν(OH)), 3293 (m; ν(NH)), 3210 (w), 3062 (m; ν(CH)ar), 3012 (w), 2924 (w), 1631 (m), 1600 (w), 1546 (m; δ(NH)), 1496 (w), 1449 (w; δ(CH)ar), 1396 (w), 1170 (s; ν(S = O)OTs), 1122 (s), 1098 (m), 1033 (s; ν(S = O)OTs), 1008 (s; ν(S = O)OTs), 908 (w), 881 (w), 813 (m; δ(ring)), 709 (w), 681 (s; ν(CS)OTs), 623 (s), 563 (s; ν(CS)OTs), 493 (w), 457 (w).

FTIR **2** (cm^{-1}): ν = 3441 (w; ν(OH)), 3293 (m; ν(NH)), 3210 (w), 3062 (m; ν(CH)ar), 3012 (w), 2924 (w), 1631 (m), 1600 (w), 1546 (m; δ(NH)), 1496 (w), 1449 (w; δ(CH)ar), 1396 (w), 1170 (s; ν(S = O)OTs), 1122 (s), 1098 (m), 1033 (s; ν(S = O)OTs), 1008 (s; ν(S = O)OTs), 908 (w), 881 (w), 813 (m; δ(ring)), 709 (w), 681 (s; ν(CS)OTs), 623 (s), 563 (s; ν(CS)OTs), 493 (w), 457 (w).

FTIR **3** (cm^{-1}): ν = 3441 (w; ν(OH)), 3293 (m; ν(NH)), 3210 (w), 3062 (m; ν(CH)ar), 3012 (w), 2924 (w), 1631 (m), 1600 (w), 1546 (m; δ(NH)), 1496 (w), 1449 (w; δ(CH)ar), 1396 (w), 1170 (s; ν(S = O)OTs), 1122 (s), 1098 (m), 1033 (s; ν(S = O)OTs), 1008 (s; ν(S = O)OTs), 908 (w), 881 (w), 813 (m; δ(ring)), 709 (w), 681 (s; ν(CS)OTs), 623 (s), 563 (s; ν(CS)OTs), 493 (w), 457 (w).

4) Thermogravimetric analyses

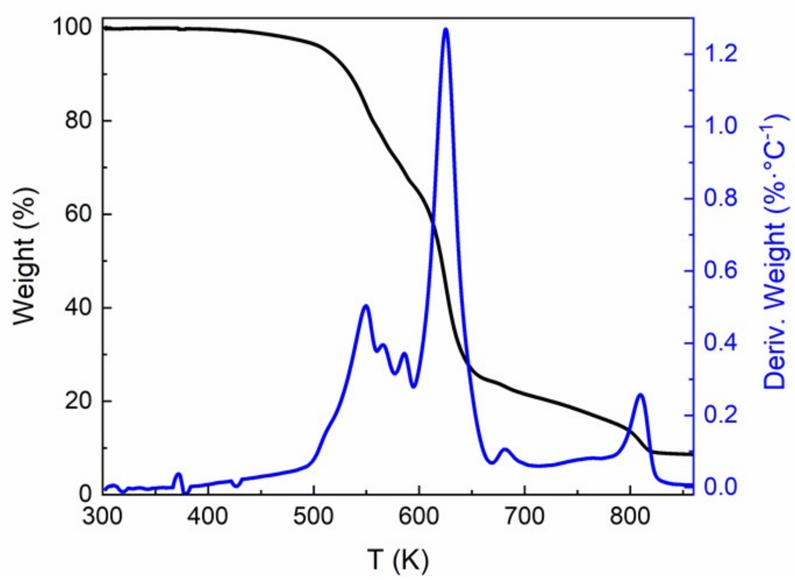

Figure S2. Thermogravimetric analysis of **1** between 300K and 873 K.

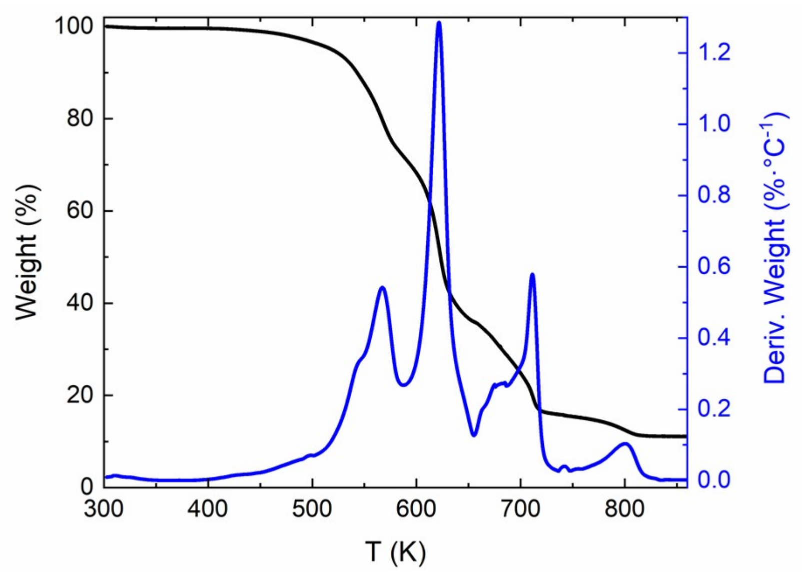

Figure S3. Thermogravimetric analysis of **2** between 300K and 873 K.

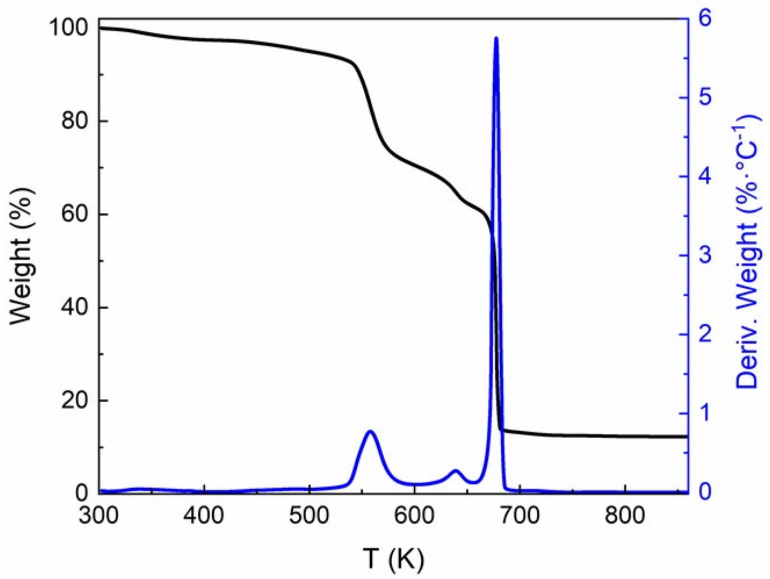

Figure S4. Thermogravimetric analysis of **3** between 300 K and 873 K.

5) Differential Scanning Calorimetry (DSC) studies

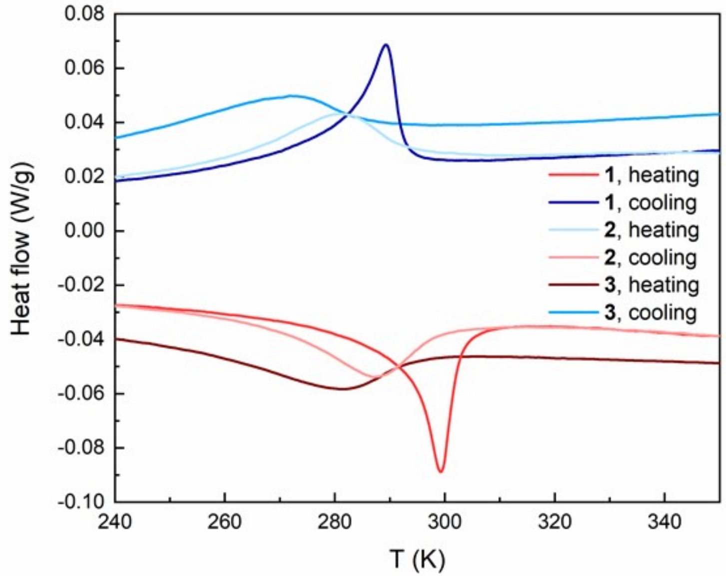

Figure S5. DSC of **1**, **2** and **3** between 230 K and 370 K.

Table S1. Enthalpy of the SCO for compounds **1**, **2** and **3**.

Compound	Enthalpy$_{\downarrow}$ (KJ/mol)	Enthalpy$_{\uparrow}$ (KJ/mol)
1	5.9	5.8
2	5.5	5.7
3	5.4	5.6

6) Dynamic Light Scattering (DLS)

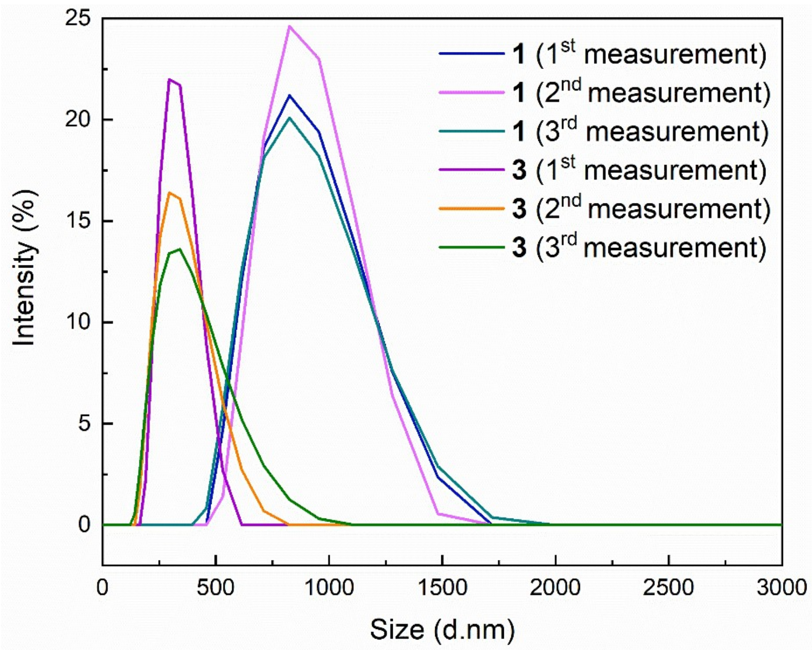

Figure S6. DLS measurements of compounds **1** and **3**. Each sample was measured three times.

Samples **1** and **3** were dispersed in tetrahydrofuran (THF) and sonicated for 30 minutes before performing the measurements. DLS measurements could not be successfully carried out for compound **2**, as it exhibits a significant polydispersion.

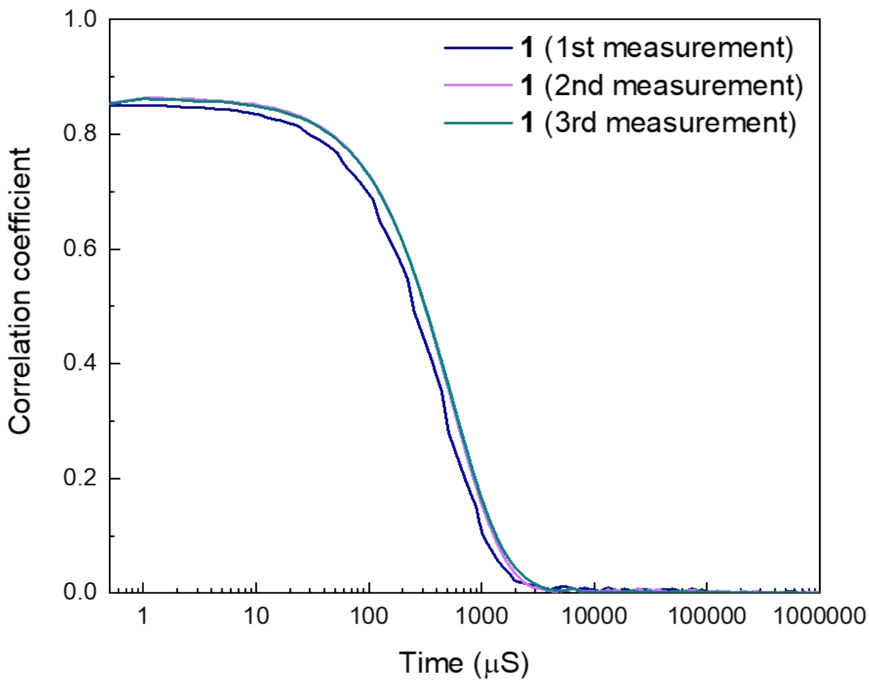

Figure S7. Correlation function of the DLS measurements of compound **1**.

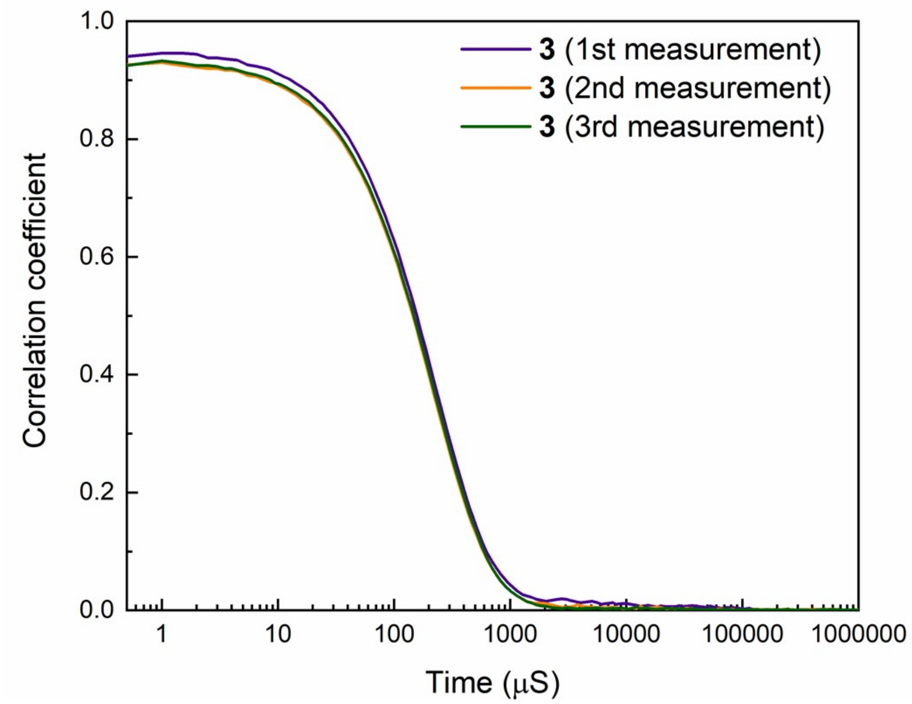

Figure S8. Correlation function of the DLS measurements of compound **3**.

7) Magnetic measurements

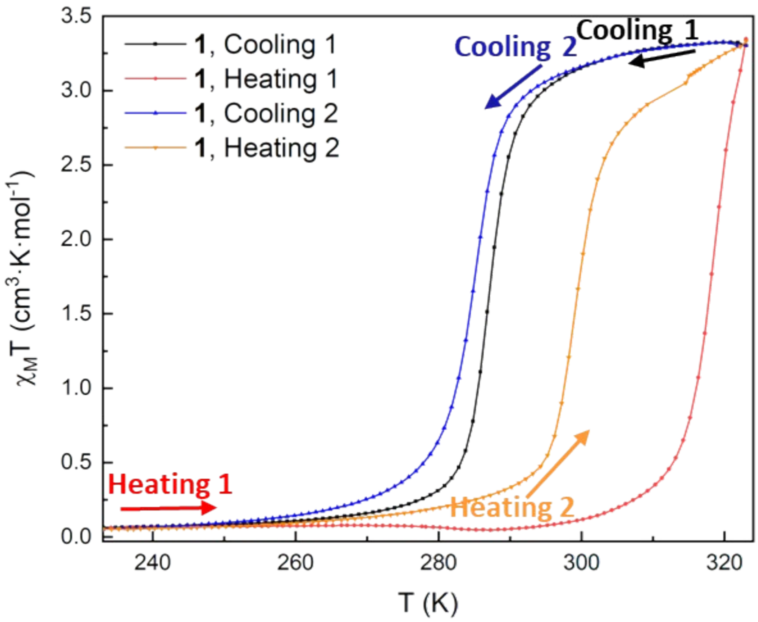

Figure S9. $\chi_M T$ measured as a function of the temperature for **1** between 230 K and 330 K.

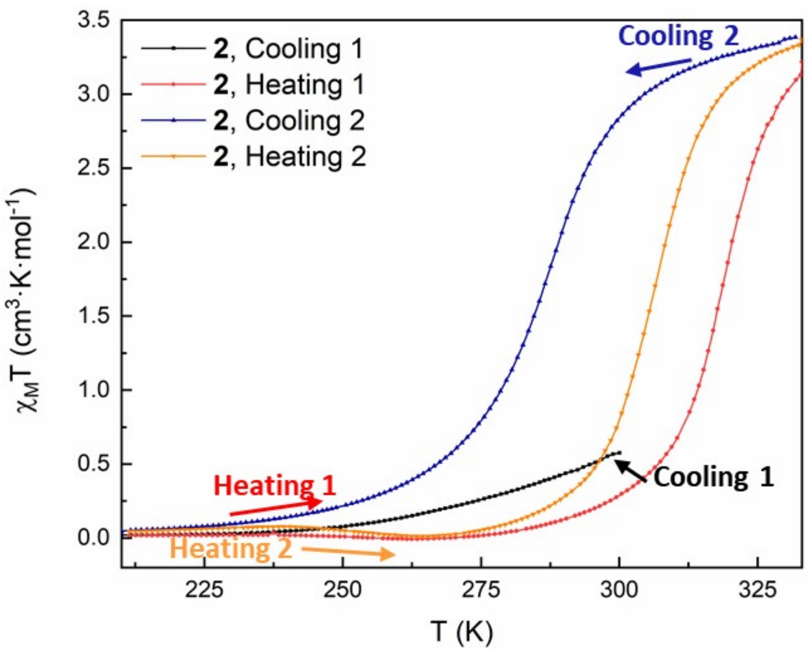

Figure S10. $\chi_M T$ measured as a function of the temperature for **2** between 230 K and 330 K.

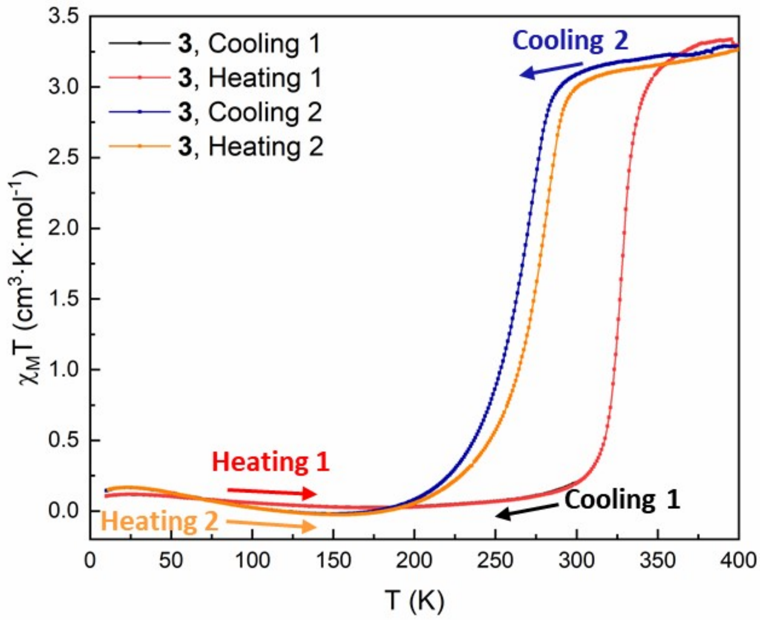

Figure S11. $\chi_M T$ measured as a function of the temperature for **3** between 10 K and 400 K.

The samples were not dried in the oven. As can be seen in the TGA plots (see section 4), **1** contains 0.1 molecules of EtOH, **2** contains 0.5, and **3** contains 0.4, which is why the first transition cycle is shifted at high temperatures in both cases.