

## Electronic Supplementary Information

### EXPERIMENTAL SECTION

#### Synthesis of compounds **1** and **2**:

The synthesis of compounds  $\{[\text{Mn}_2(\text{NITIm})_3]\text{ClO}_4\}_n$  (**1**) and  $\{[\text{Mn}_2(\text{NITIm})_3]\text{BF}_4\}_n$  (**2**) has been already reported in our previous articles.<sup>1, 2</sup>

**Caution!** Although not encountered in these experiments, perchlorate salts are potentially explosive and as such, only a small amount of the materials should be prepared at a time and should be handled with care.

#### Pressure magnetic measurements:

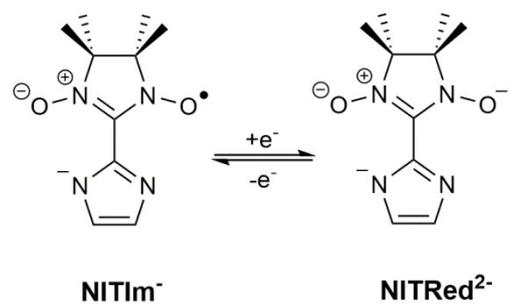
Magnetic susceptibility was measured on a MPMS-5 SQUID magnetometer under a magnetic field of 1000 or 5000 Oe in a temperature range of 2-350 K in settle mode. A cylinder piston-type of pressure cell in copper-beryllium LPC-15 (Japan ElectroLAB) was used for applying external pressure on the polycrystalline powder.<sup>3, 4</sup> A Daphne 7373 oil was used as a medium transmitting the hydrostatic pressure.<sup>5, 6</sup> Diamagnetic contributions of the Cu-Be cell and oil were corrected for data processing as well as diamagnetism of atoms according to Pascal's additive scheme.<sup>6</sup> External pressure applied varied in between  $10^{-4} \text{ GPa} \leq P \leq 0.2 \text{ GPa}$  depending on the sample. The pressure applied to the sample is calibrating by using the superconductivity transition of high purity tin placed inside the cell.<sup>7, 8</sup> The pressure ( $P$ ) was determined by the equation  $T_s(P) = T_s(P_0) - \alpha P$ , where  $\alpha$  is equal to  $0.365 \text{ K.GPa}^{-1}$ ,  $T_s(P_0)$  is the temperature of the Sn transition at atmospheric pressure and  $T_s(P)$  is the temperature of the Sn transition at applied pressure. The accuracy of pressure calibration was  $\pm 0.025 \text{ GPa}$ . The high sensitivity of compounds **1** and **2** to pressure made really difficult the good determination of pressure values lower than 0.1 GPa. A correction for the inner decrease in the pressure of liquid or solidified oil cooled from 300 to 2 K, which reaches 0.15–0.20 GPa for the pressure-transmitting medium Daphne 7373 oil,<sup>3</sup> was not applied.

The magnetic data for complexes **1** and **2** had good reproducibility for the measurements of the same sample exposed to repeated cooling-heating cycles, of the gradually or quickly cooled samples and for experiments with samples of various dispersities and batches from different synthesis. Magnetic susceptibility measurements in pressure cell were carried out at a rate of 1K/min in the temperature region associated with magnetic

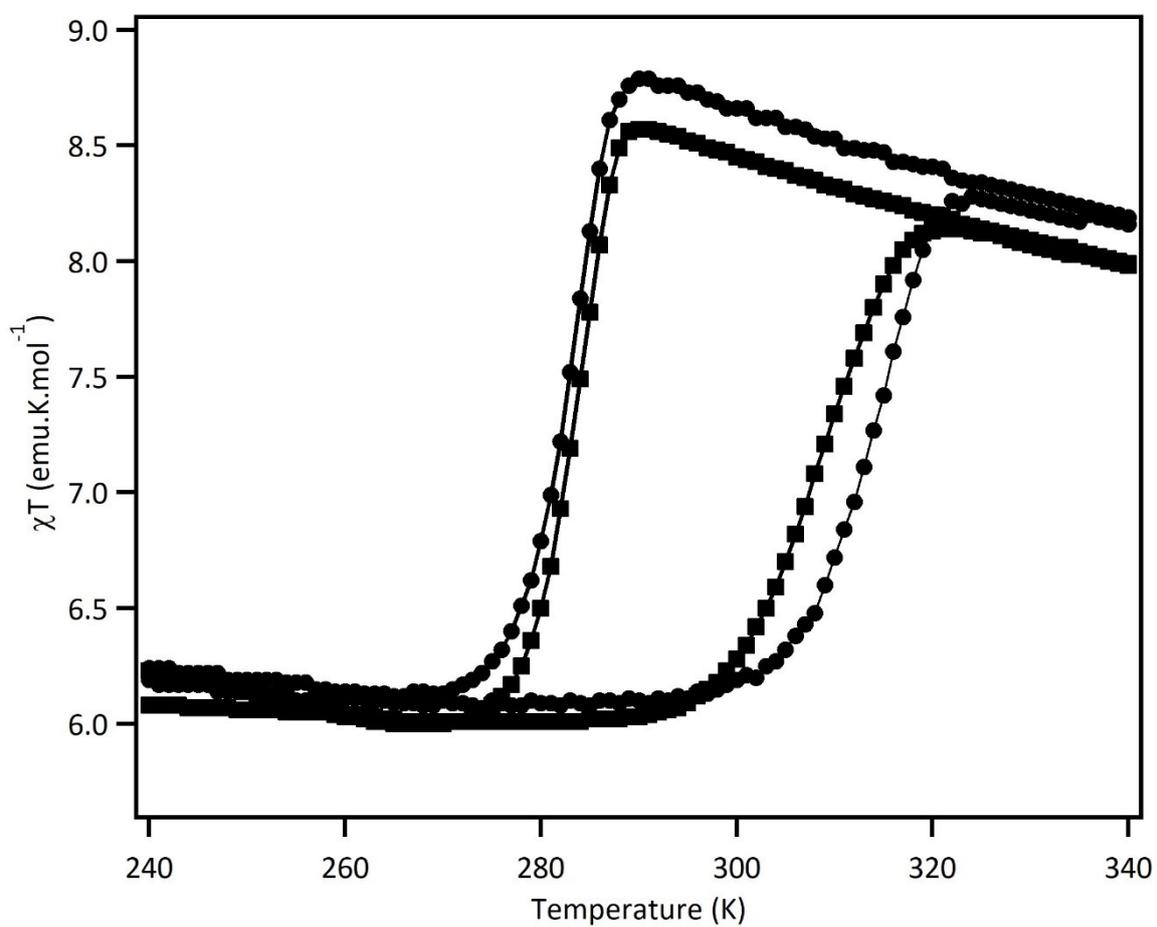
anomaly (200-350 K) and 5 K/min in the rest of the temperature range both the cooling and warming settle SQUID modes (delay 10 sec after reaching constant temperature, 3 scans per each temperature point). Samples were measured in gelatin capsule in the same heating settle mode before being placed in a pressure cell to provide a reference signal for applying a correction for Cu-Be cell and oil contributions. When the pressure decreases to its initial value, the  $\chi T(T)$  dependence acquires the same form as before the pressure increase. Small differences are attributed to a sample drift, possibly expelled outside the scanned space of the pressure cell, which was not taken into account for data processing (Fig. S1, S2). That allows us to assume that the quenching, crystals size effects, thermostatic abnormalities, and/or effect of the pressure cell body and Daphne7373 oil signals are minimized.

#### **Pressure Raman spectroscopy:**

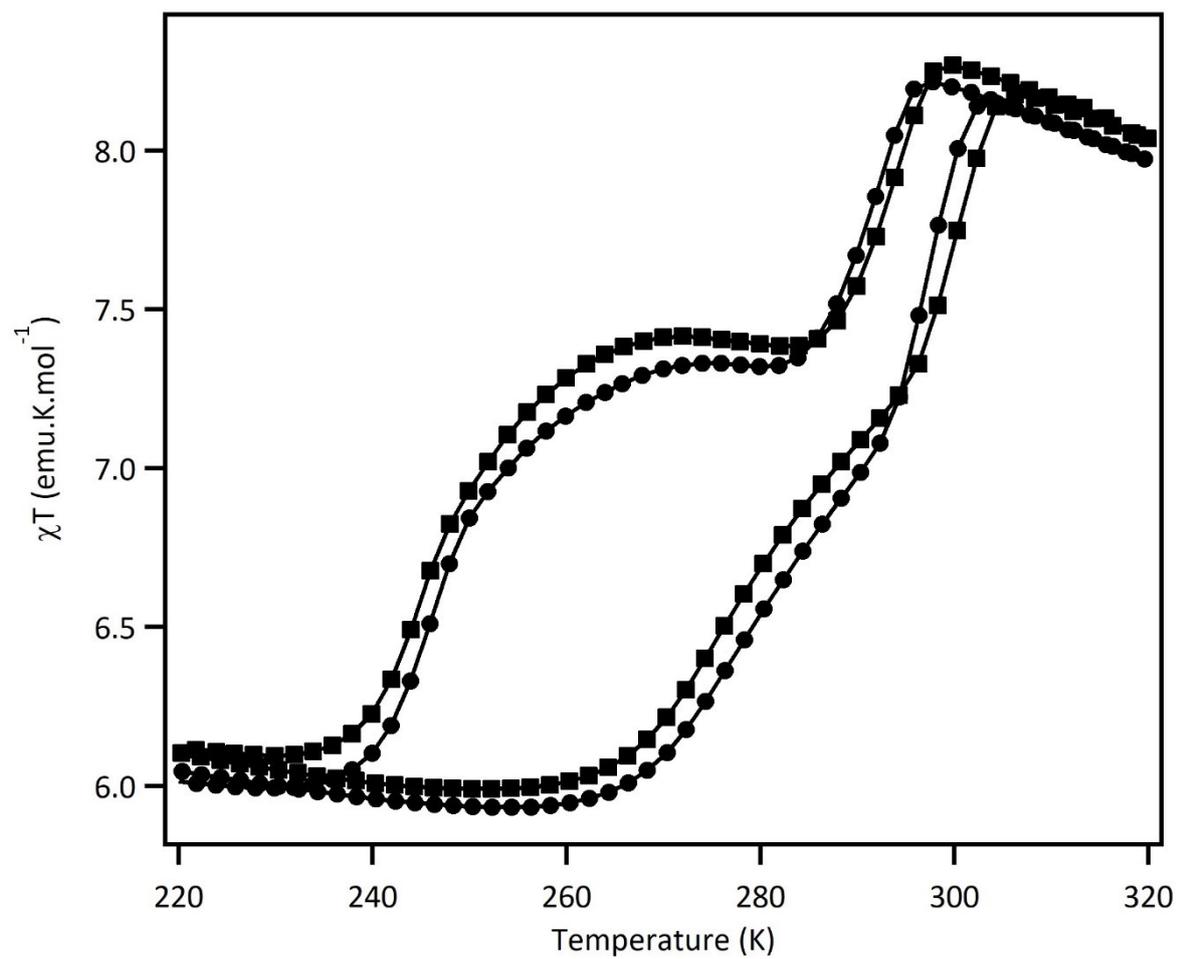
Raman spectra were measured using a Renishaw InVia spectrometer coupled to an imaging microscope (Leica) and argon ion or diode lasers. The excitation wavelengths used were 514 nm. Pressure was applied by a gasketed diamond-anvil cell (DAC, High-Pressure Diamond Optics). The crystals are loaded in the gasket in a Nujol oil medium, for hydrostatic pressure transmission. Pressure was calibrated thanks to the piezo-dependence of Ruby luminescence contained in the cell.<sup>9</sup> All luminescence spectra were corrected by calibration with a tungsten lamp to adjust for system response.



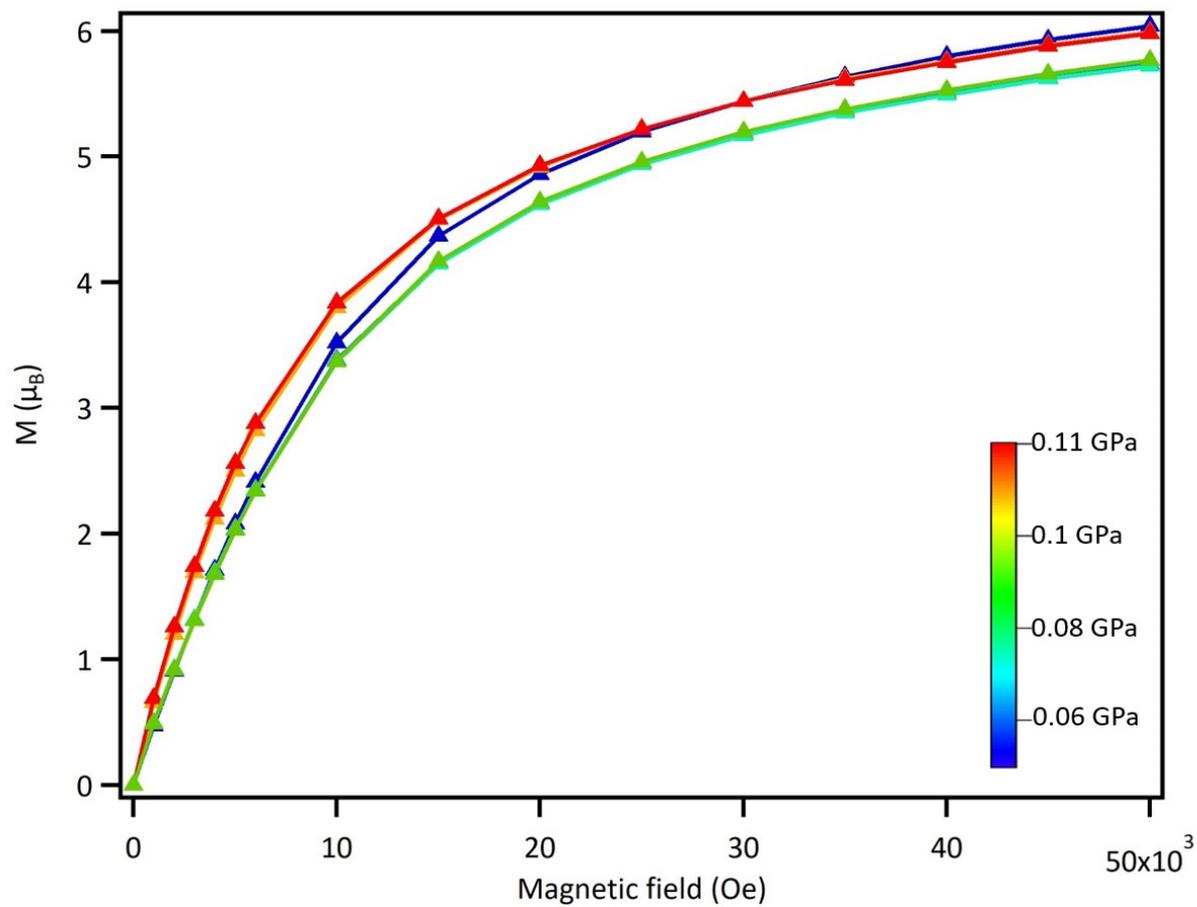
Scheme S1



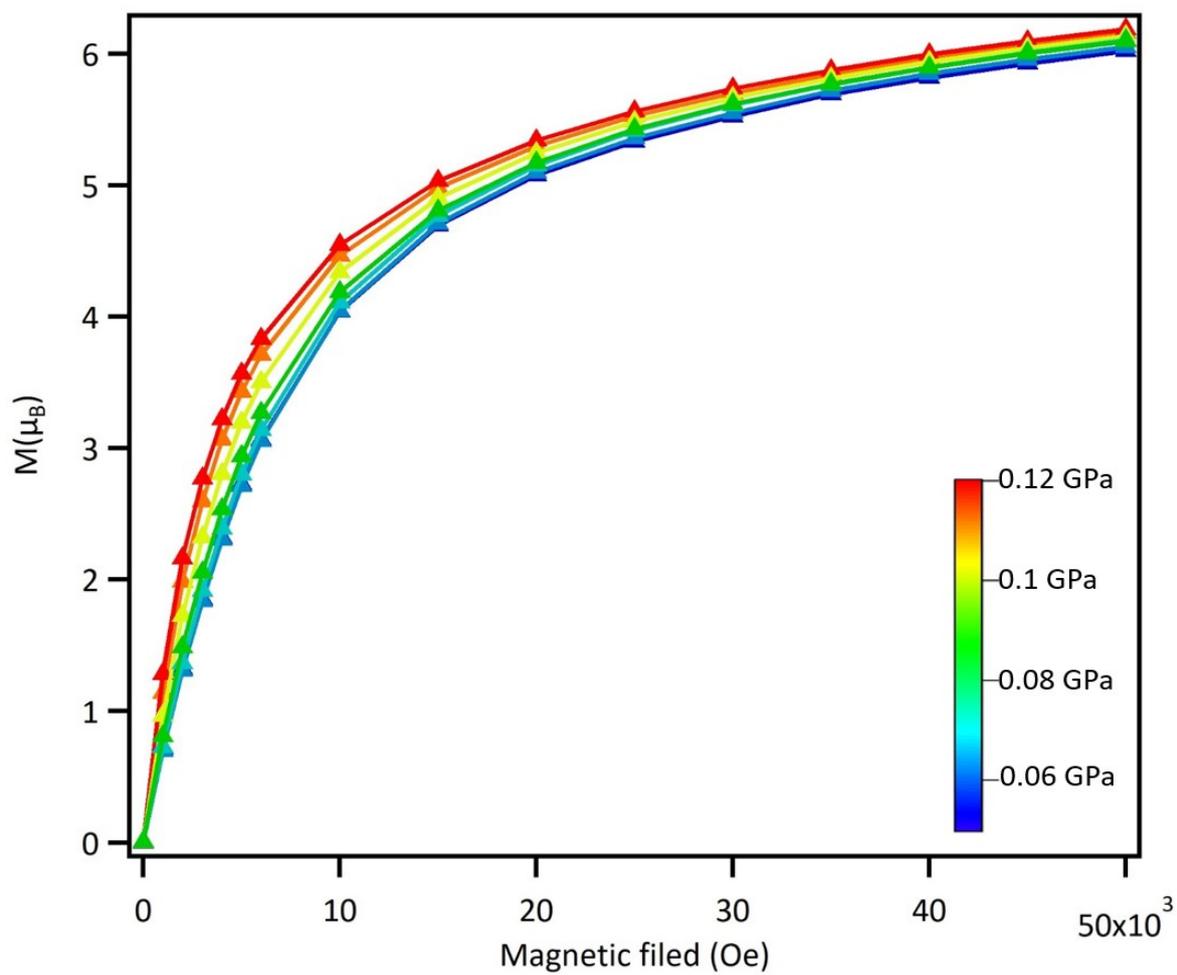
**Figure S1.**  $\chi T$  vs  $T$  curves of compound **1** before applying pressure (●) and after decompression (■). Solid lines only join the data points.



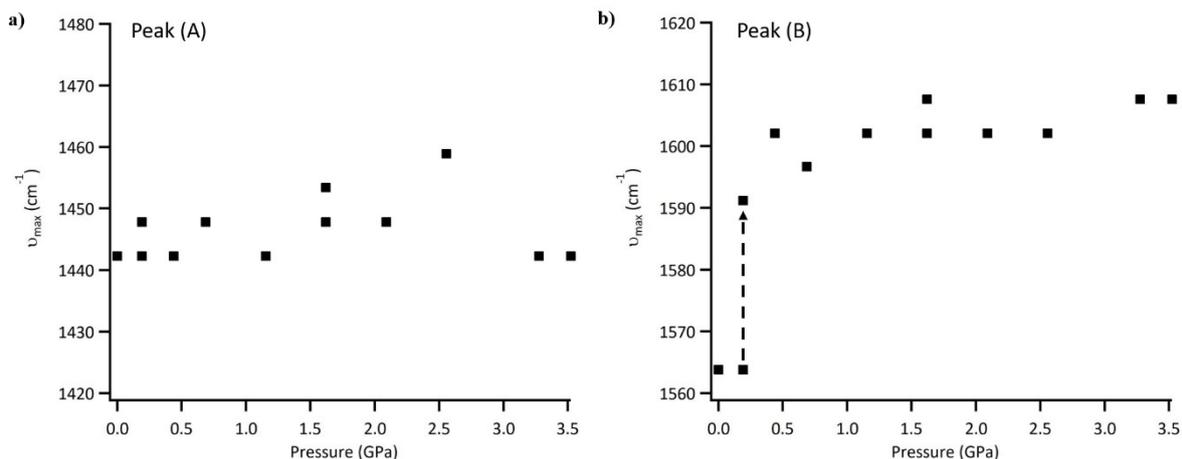
**Figure S2.**  $\chi T$  vs  $T$  curves of compound **2** before applying pressure (-●-) and after decompression (-■-). Solid lines only join the data points.



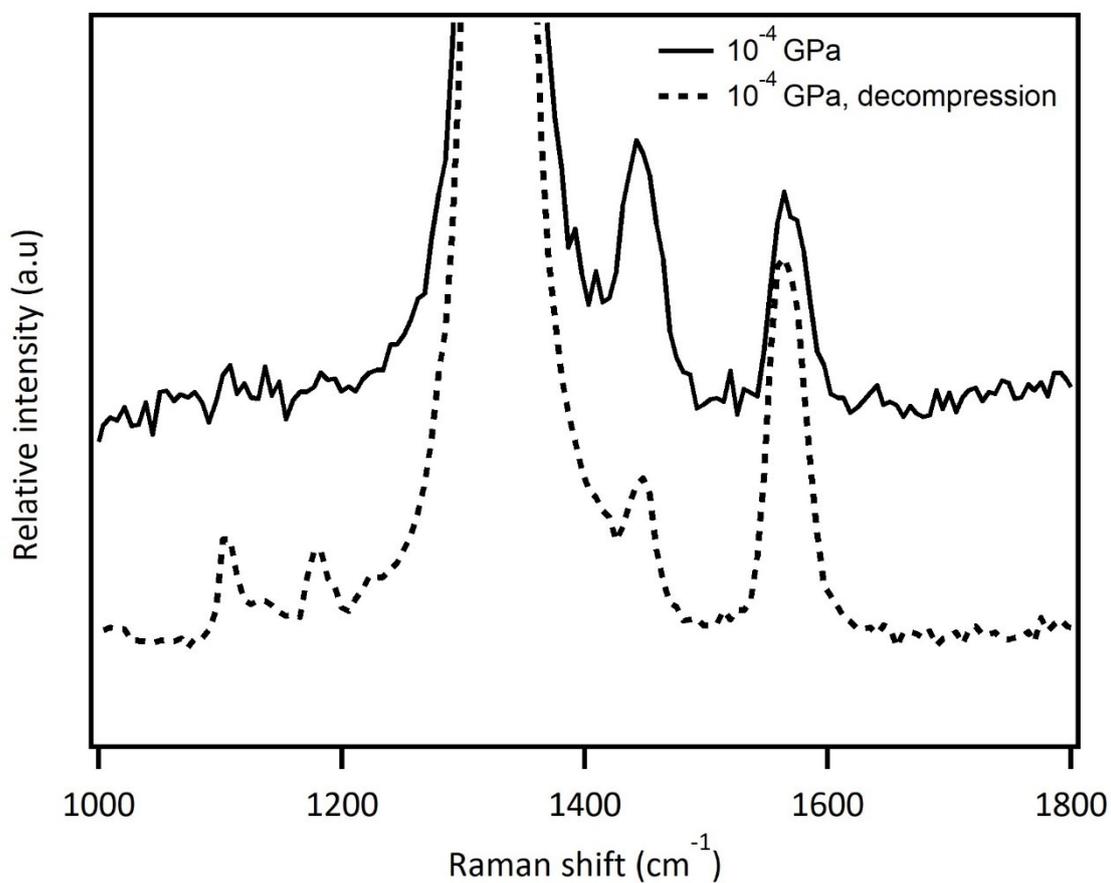
**Figure S3.** Magnetization of compound **1** at 2K, as function of the applied external magnetic fields and for different pressure values.



**Figure S4.** Magnetization of compound **2** at 2K, as function of the applied external magnetic fields and for different pressure values.



**Figure S5.** Maxima of Raman peak frequency in function of applied pressure of compound **1**.



**Figure S6.** Raman spectra of compound **1** measured at  $10^{-4}$  GPa before compression (line) and after decompression (dotted line) at room temperature under an excitation wavelength of 514 nm. The most intense peak at  $1330 \text{ cm}^{-1}$  in each spectrum corresponds to the diamond characteristic band.

## References

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