Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information

Experimental details

Compounds **1** and **2** were prepared by a solid state procedure described in [1] starting from stoichiometric mixture of chemically grade $(NH_4)_2HPO_4$, CuO, and $BaCO_3$ (2% excess) or $CaCO_3$ (0.5% excess) correspondingly. The obtained powders were pressed in pellets, sintered in air at 1150°C and finally annealed at 900°C for 2 hours in flowing oxygen in order to enhance fraction of Cu^{3+}. Powder X-ray diffraction was conducted on a Rigaku D/MAX 2500 (CuKα radiation, 2θ range 15 – 80 deg., step 0.02 deg.). Crystal cell parameters were calculated in the full-profile refinement using JANA2006 program. Raman spectra were recorded on a Renishaw in Via Raman Microscope with a laser wavelength of 514 nm in the shift range 100 – 1400 cm^{-1}. Magnetization was measured on a Quantum Design SQUID MPMS-VSM in the temperature range 1.8 – 100 K under dc magnetic fields up to 70 kOe. The field was fixed at a certain value while the temperature was slowly increased and then decreased in the measurement diapason. Relaxation of magnetization was investigated by SQUID AC-susceptibility on the same device in the frequency range 0.1 – 945 Hz with an ac field amplitude of 2.5 – 3 Oe in the temperature range 2 – 12 K and under dc fields of up to 10 kOe. Samples for the measurements were rectangular pieces of ceramics 30 – 60 mg in weight fixed to a quartz sample holder by glue. Ac susceptibility of **1** was also measured on the powdered sample (ca. 190 mg) loaded in a quartz-glass tube in order to get higher precision. Magnetization values were corrected for core diamagnetism (Pascal's constants), susceptibility of the glue and the quartz-glass tube.

[1] P. E. Kazin, M. A. Zykin, Y. D. Tretyakov, M. Jansen, *Russ. J. Inorg. Chem.* **2008**, *53*, 362 – 366.

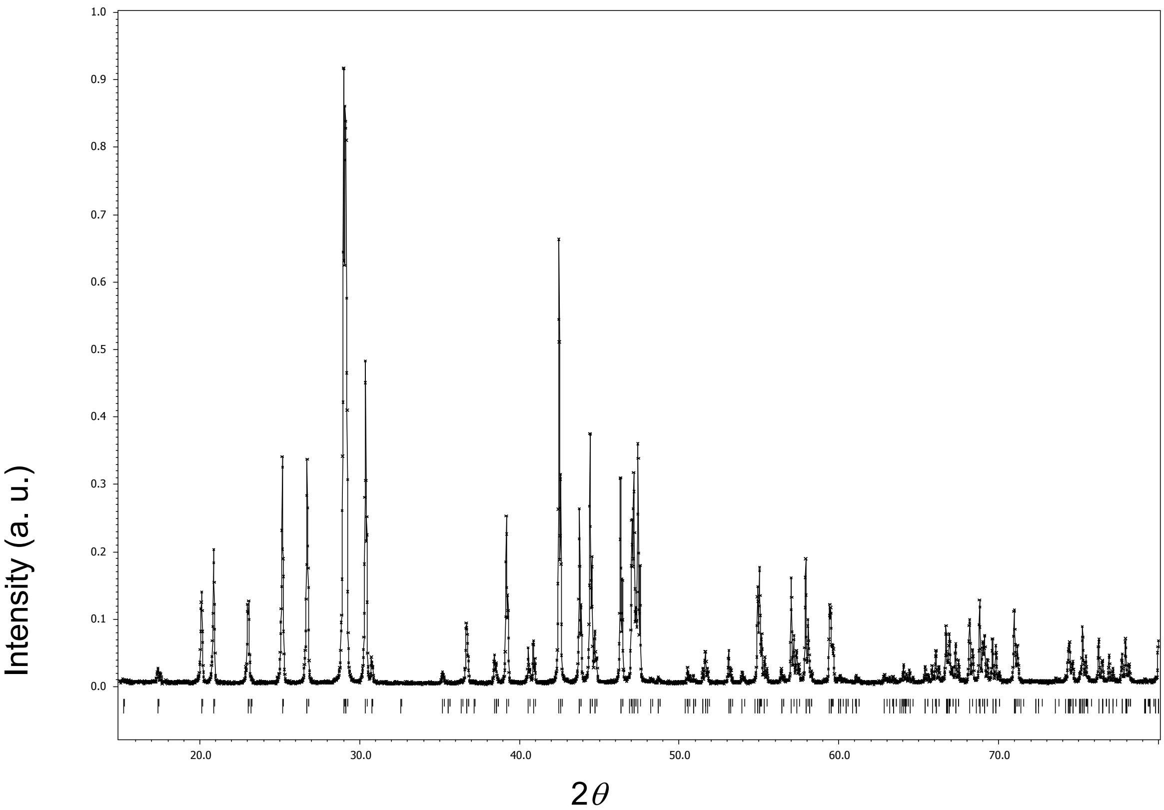

Figure S1. X-ray diffraction pattern of **1** and calculated positions of Bragg reflections below, space group P6_3/m, a = 10.1920(2) Å, c = 7.7218(2) Å, V = 694.66(3) $Å^3$.

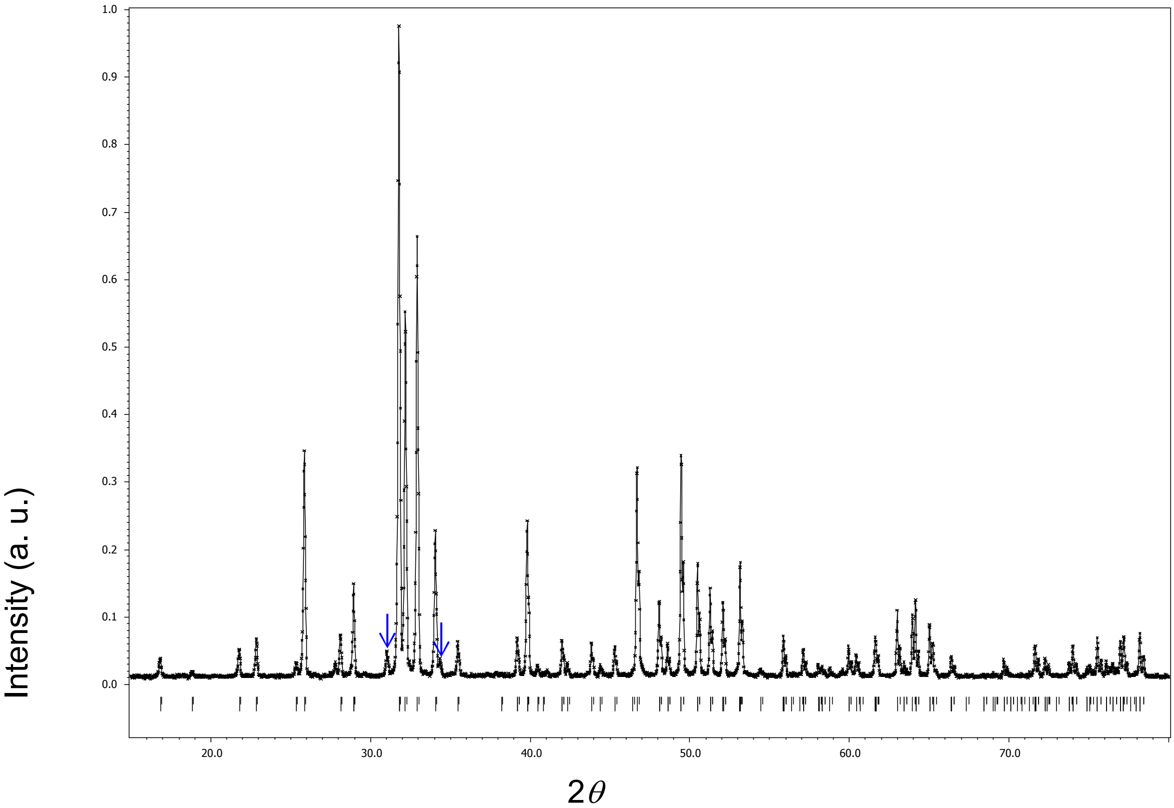

Figure S2. X-ray diffraction pattern of **2** and calculated positions of Bragg reflections below, space group $P6_3/m$, a = 9.4236(1) Å, c = 6.8892(1) Å, V = 529.82(1) Å^3. Arrows indicate the reflections of the admixture phase β-$Ca_3(PO_4)_2$.

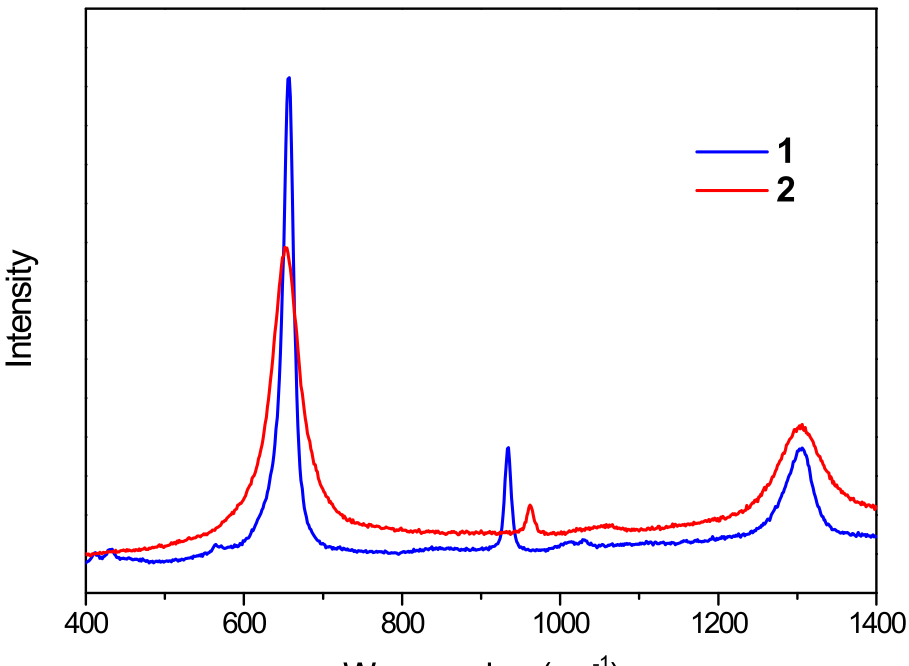

Figure S3. Raman spectra of **1** and **2**. A sharp peak at 934 cm^{-1} (**1**) and 962 (**2**) corresponds to ν_1 of PO_4-group.

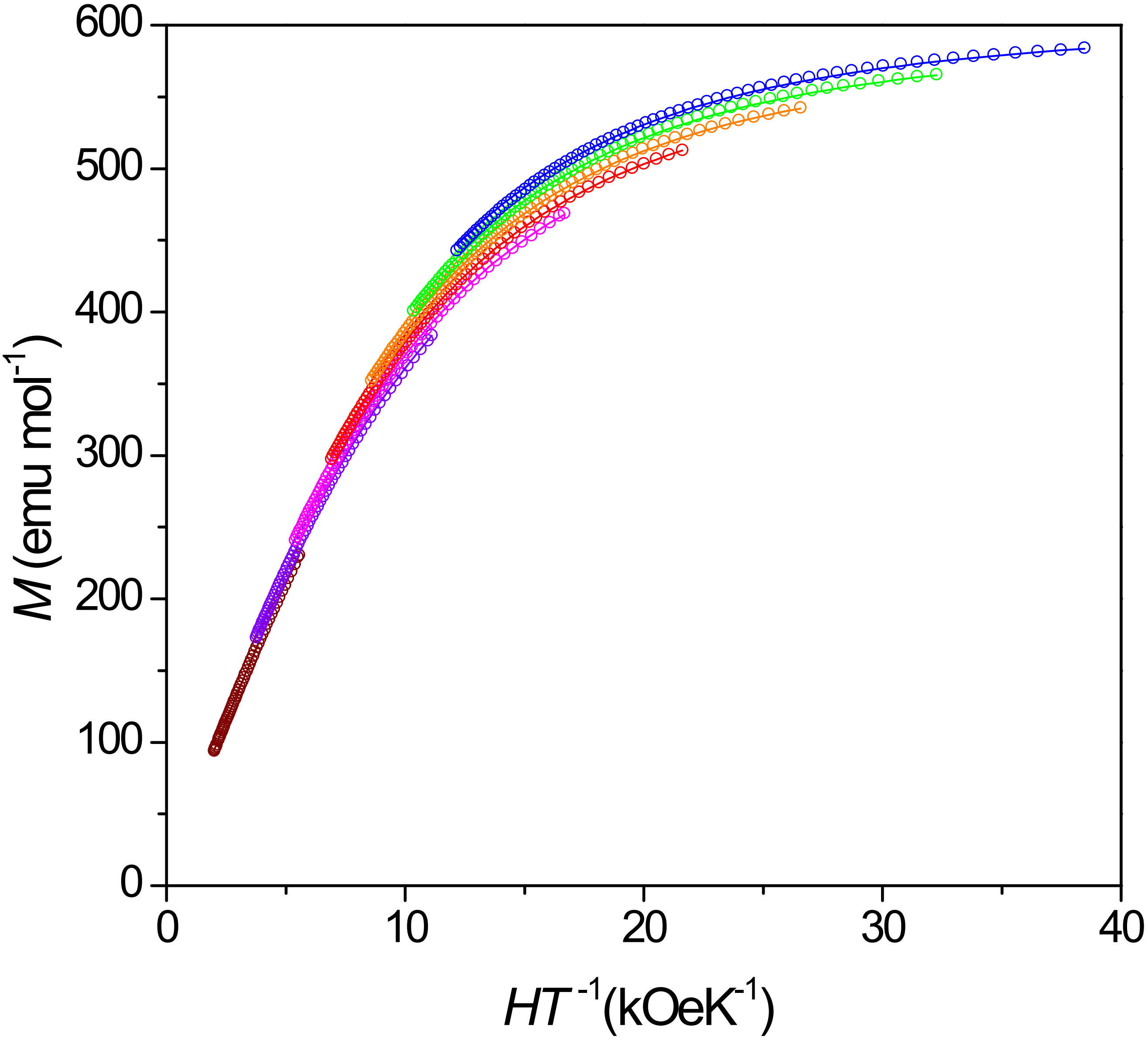

Figure S4. Magnetization in $M(T)$-series in the temperature range 1.8 – 5 K under fixed dc fields from 10 to 70 kOe (brown, violet, magenta, re, orange, green, blue), step 10 kOe, *vs*. HT^{-1} of **1**. Experimental points, circles; fitted, lines.

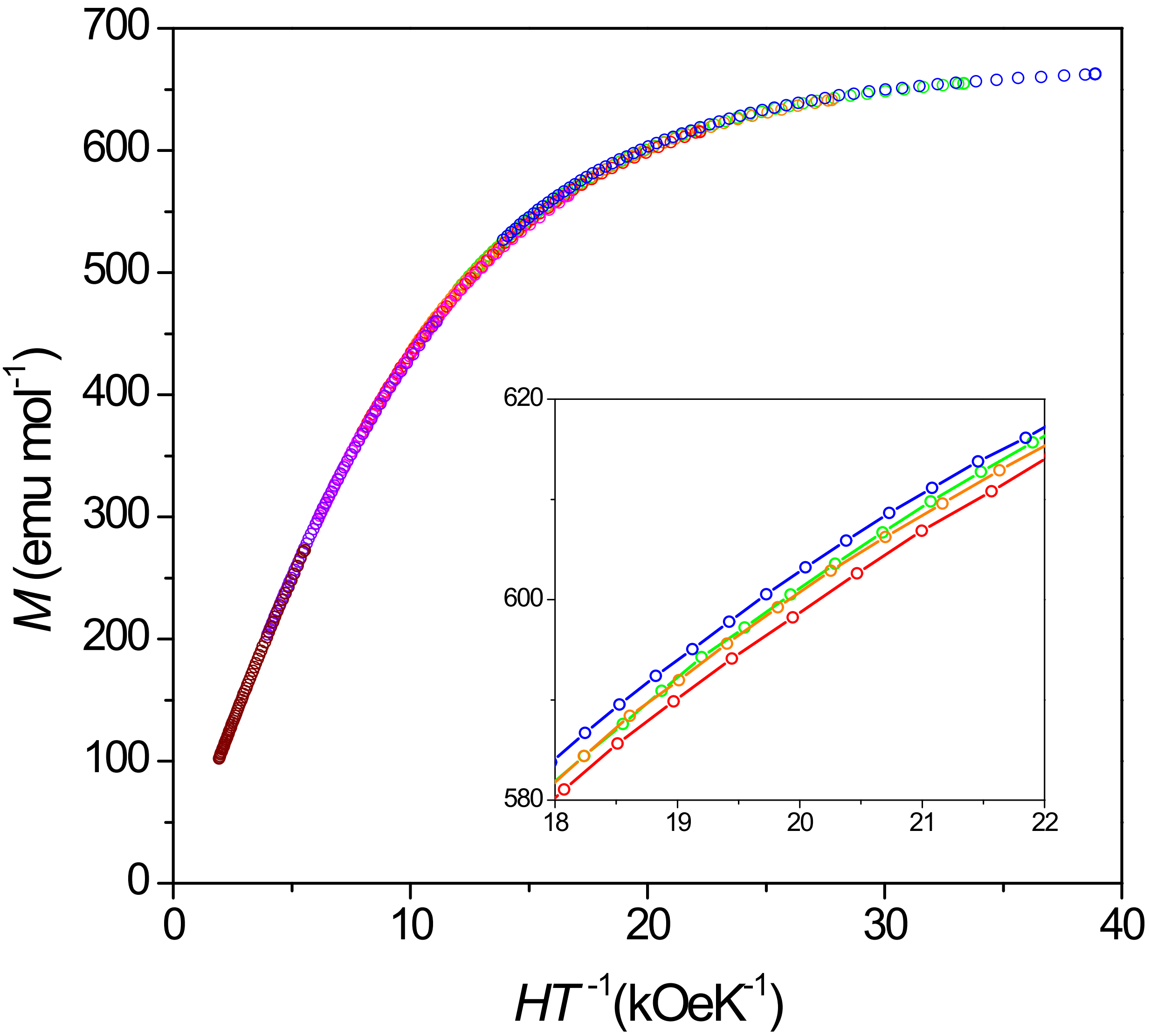

Figure S5. Magnetization in *M*(*T*)-series in the temperature range 1.8 – 5 K under fixed dc fields from 10 to 70 kOe (brown, violet, magenta, re, orange, green, blue), step 10 kOe, *vs*. HT^{-1} of **2**. Experimental points, circles. Insert: enlarged area of intermediate fields; experimental points, circles; lines drawn to guide the eye.

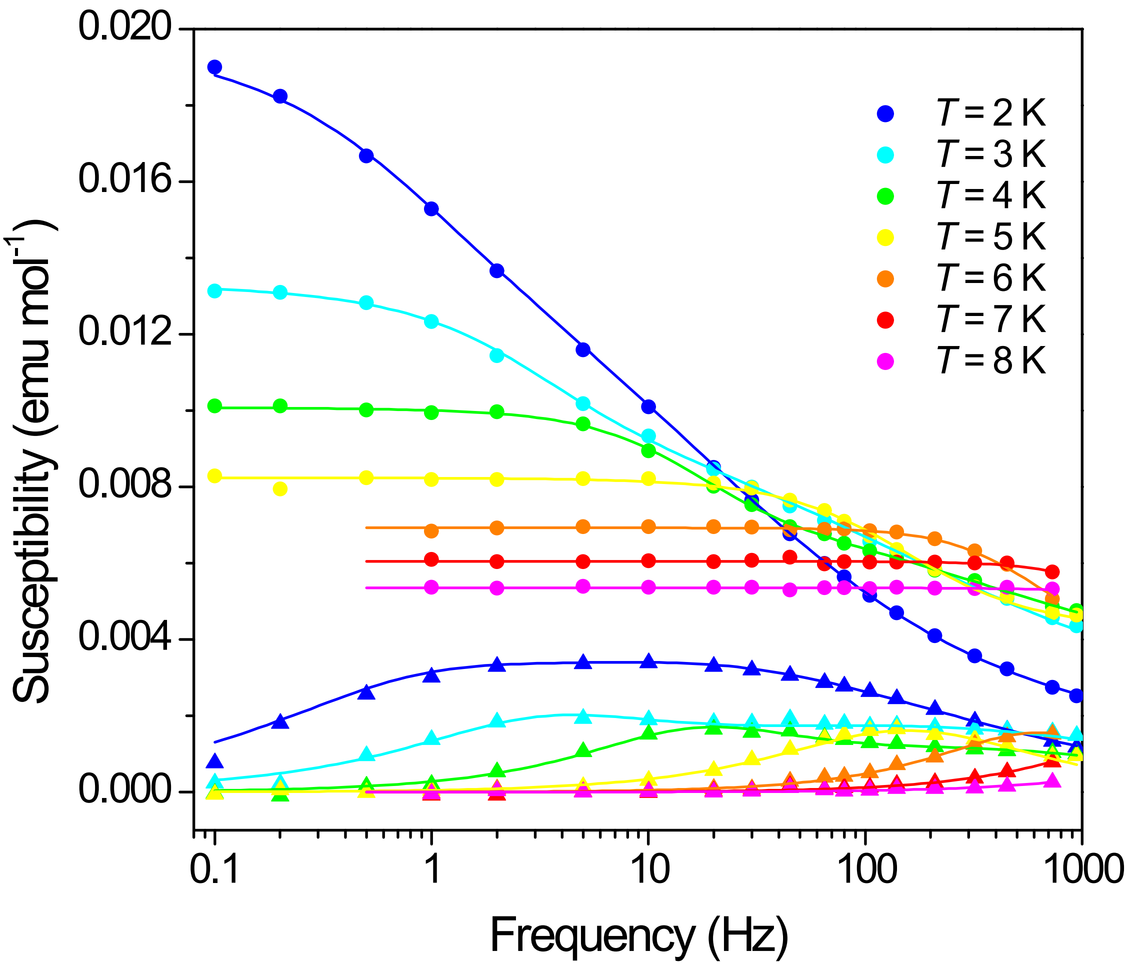

Figure S6. In-phase- (circles) and out-of-phase (triangles) susceptibility of **1** *vs*. ac field frequency under a dc field of 1.5 kOe in the temperature range 2 – 8 K. Lines represent fitting curves for two relaxation pathways.

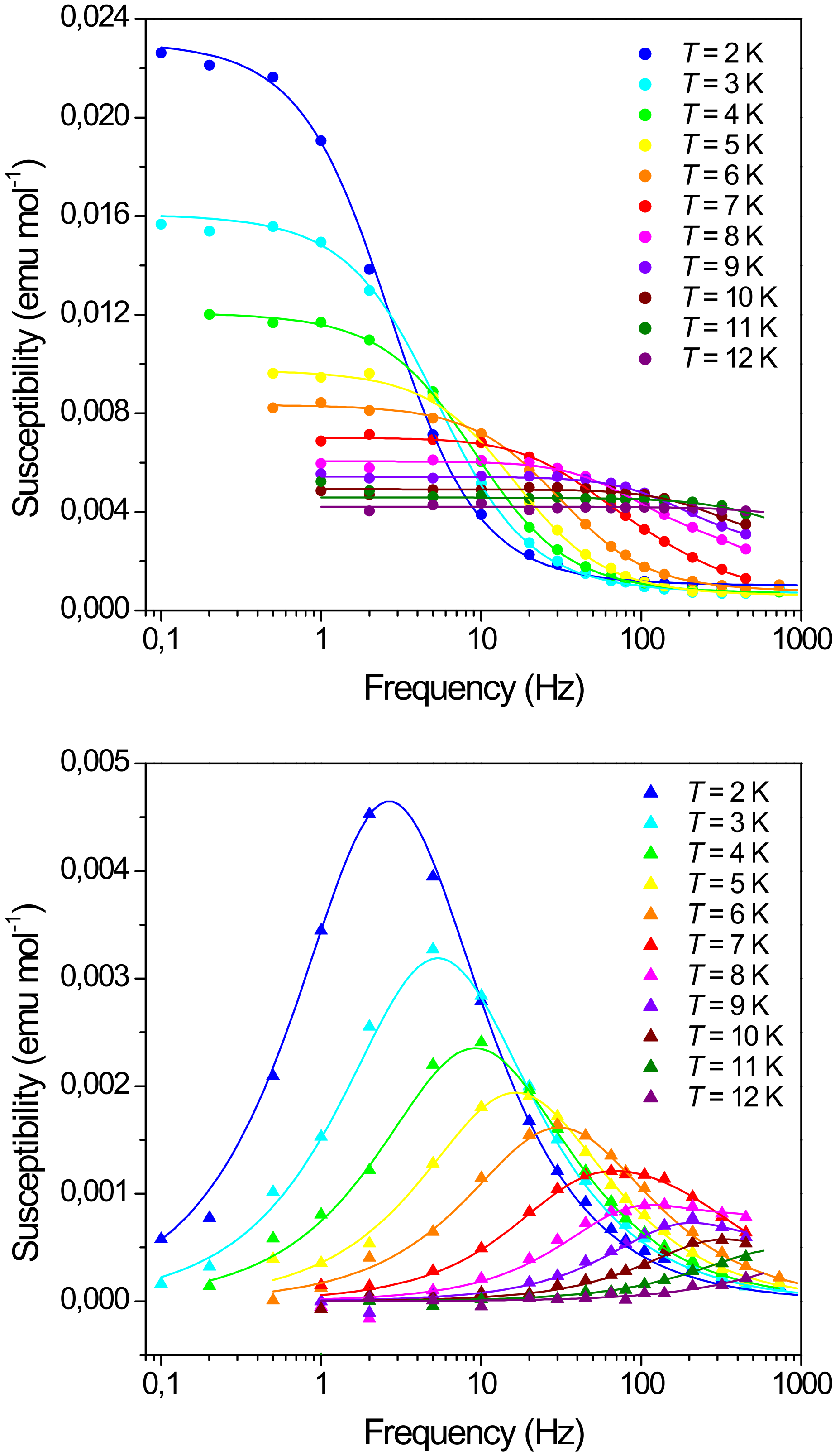

Figure S7. In-phase (top) and out-of-phase (bottom) susceptibility of **2** *vs*. ac field frequency under a dc field of 6 kOe in the temperature range 2 – 12 K. Lines represent fitting curves for single relaxation pathway (T = 2 – 6 K) and for two relaxation pathways (T > 6 K).

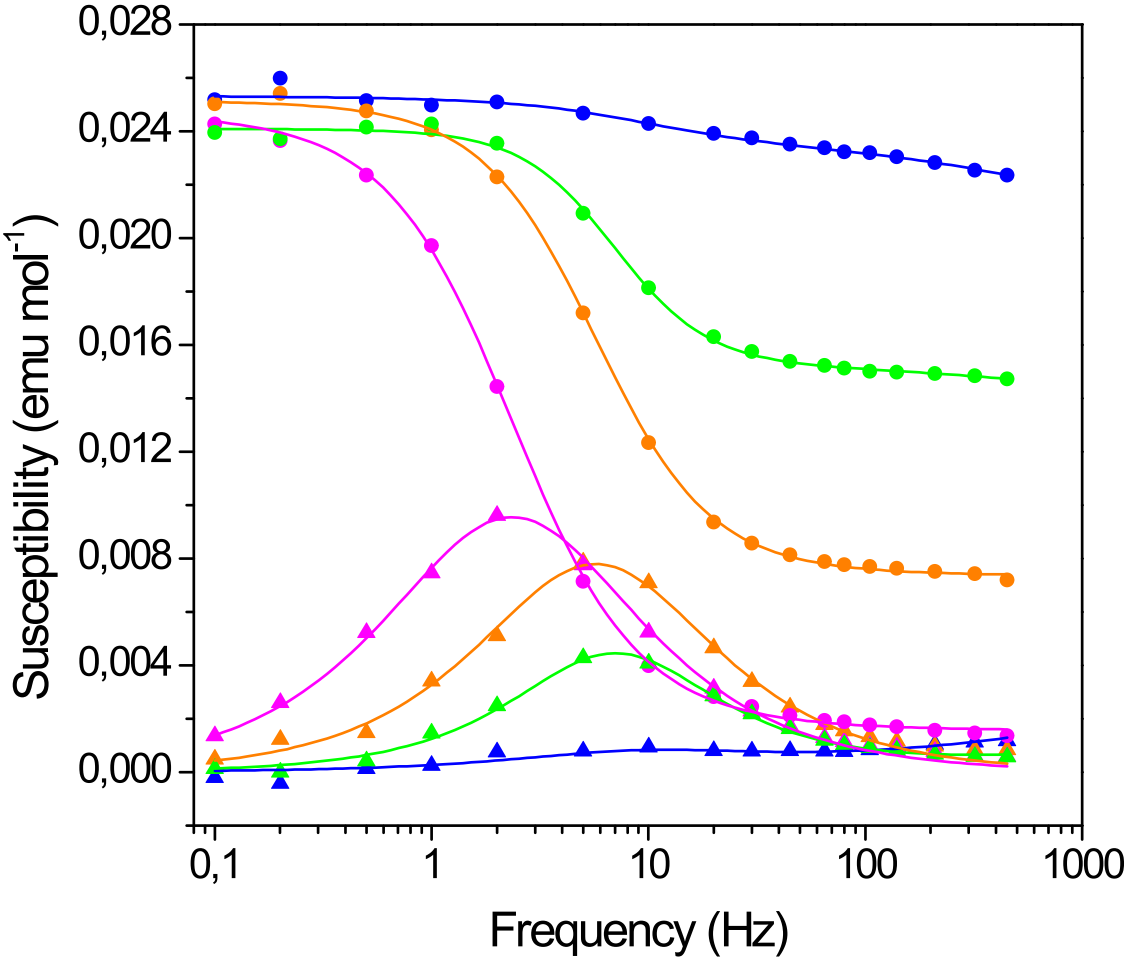

Figure S8. In-phase (circles) and out-of-phase (triangles) susceptibility of **2** *vs*. ac field frequency at a temperature of 2 K under a dc field of 0.15 (blue), 0.5 (green), 1 (orange), and 5 (magenta) kOe. Lines represent fitting curves for single relaxation pathway (0.5 – 5 kOe) and two relaxation pathways (0.15 kOe).

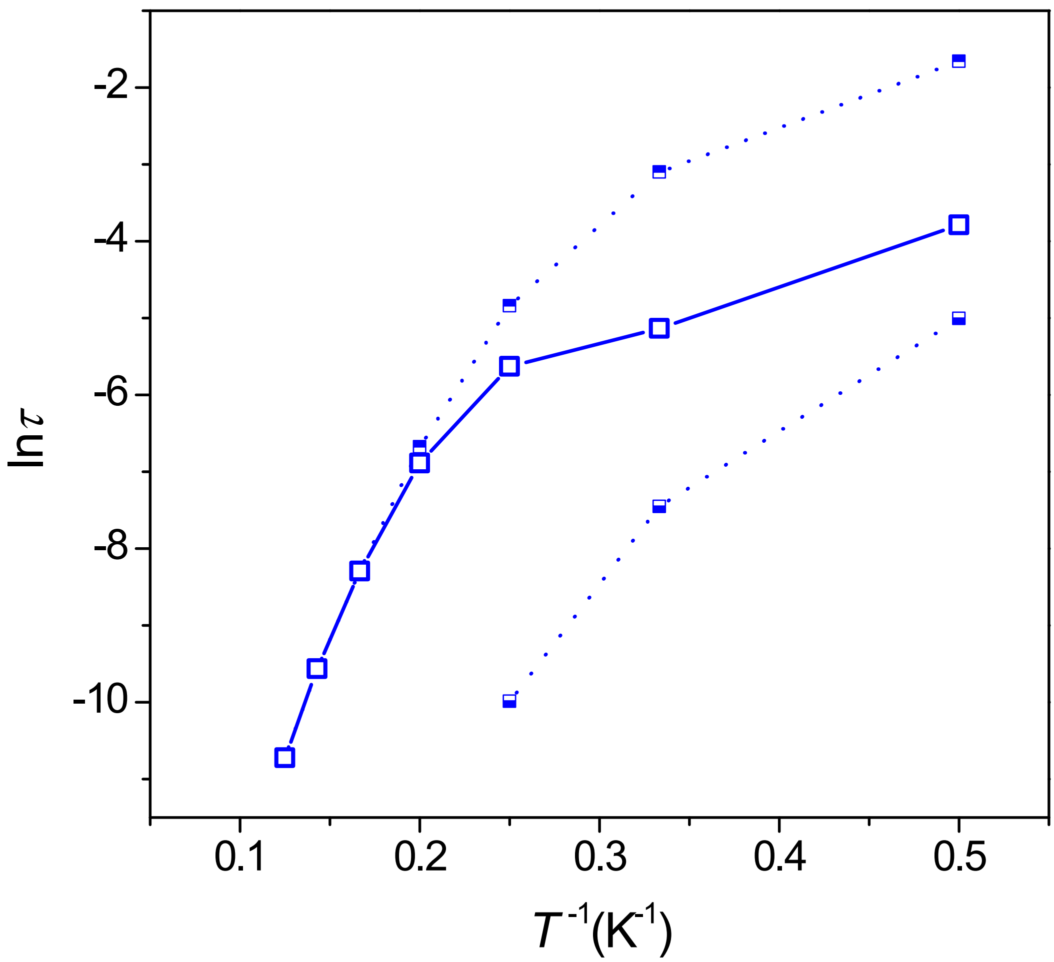

Figure S9. Arrhenius plots for **1** for the relaxation times τ (open squares), τ_1 (filled top squares), and τ_2 (filled bottom squares). Lines drawn to guide the eye.

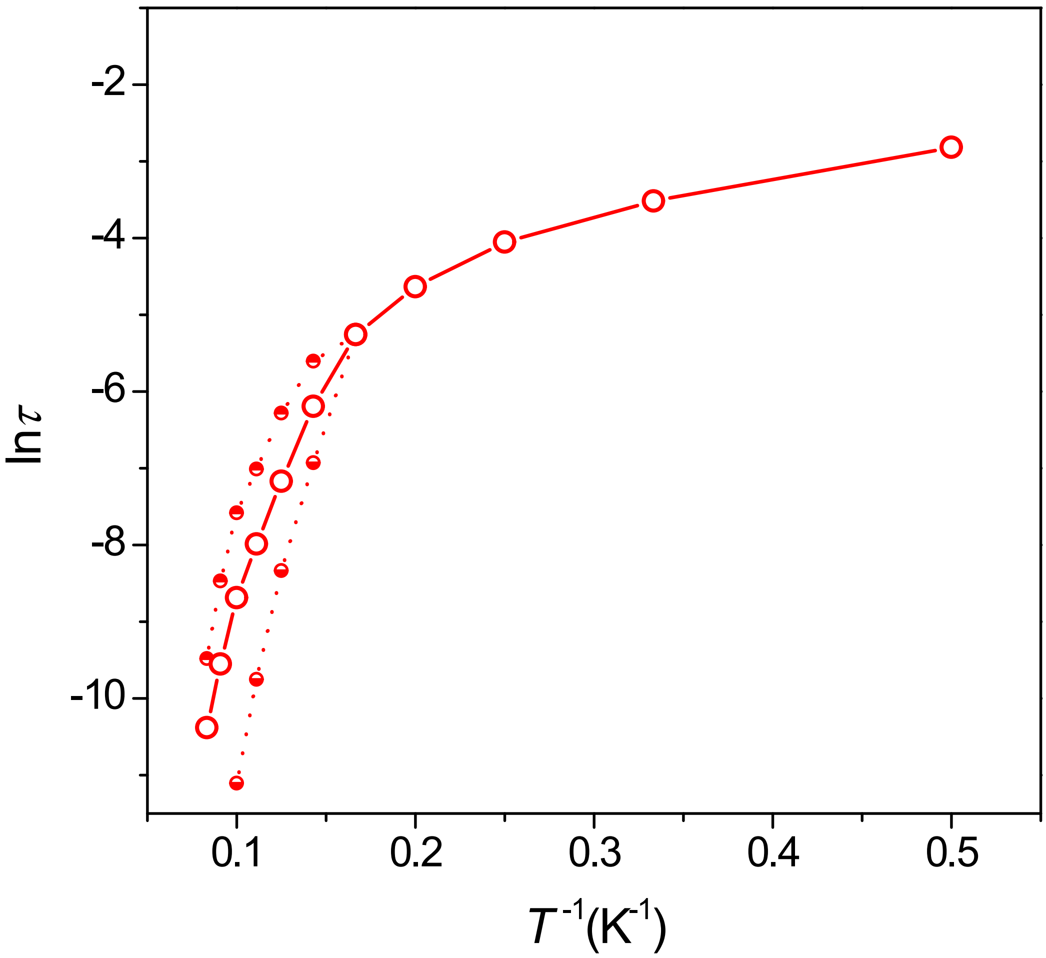

Figure S10. Arrhenius plots for **2** for the relaxation times τ (open circles), τ_1 (filled top circles), and τ_2 (filled bottom circles). Lines drawn to guide the eye.