Supplementary Information

Temperature controlled formation of polar copper phosphonate showing large dielectric anisotropy and dehydration-induced switch from ferromagnetic to antiferromagnetic interactions

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Experimental Section

Materials and Measurements. The reagents employed were commercially available and used without further purification. The 2-carboxyphenylphosphonic acid (2-cppH_3) was synthesized by the Arbuzov reaction.[1] Elemental analyses (EA) were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a Bruker Tensor 27 spectrometer with KBr pellets. Thermogravimetric analyses were performed with a METTLER TOLEDO TGA/DSC 1 instrument in the ranger of 30-500˚C under a nitrogen flow at a heating rate of 10 ^{o}C/min for all measurements. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 advance diffractometer with Cu-*Kα* radiation (λ = 1.54056 Å) and Mo-*Kα* radiation (λ = 0.71073 Å). The magnetic susceptibility data were recorded on polycrystalline samples using a vibrating sample magnetometer (VSM) of the Quantum Design MPMS SQUID-VSM system. The data were corrected for diamagnetic contributions of both the samples holder and the compound obtained from Pascal's constant.[2]

Synthesis of $Cu_3(2\text{-}cpp)_2(H_2O)_5$ (1). A mixture of $CuCl_2 \cdot 2H_2O$ (0.0171g, 0.1 mmol), 2-cppH_3 (0.1 mmol, 0.0202 g) in H_2O (8 mL), adjusted to 2.8 by addition of dilute piperazine solution (1.0 M), was placed in a Teflon-lined stainless steel vessel. The mixture was sealed and heated at 100 ^{o}C for 3 days, and then the reaction system was cooled to room temperature. The blue plate-like crystals were obtained in a yield of 55% (based on Cu). Elemental analysis (%) calcd. for $C_{14}H_{18}O_{15}P_2Cu_3$: C 24.74, H 2.65. Found: C 24.83, H 2.29. IR (KBr, cm^{-1}): 3406 (br), 3276 (br), 3059 (w), 2925 (w), 1580 (s), 1562 (m), 1537 (w), 1486 (w), 1469 (w), 1443 (w), 1422 (m), 1406 (s), 1384 (w), 1259 (w), 1143 (s), 1117 (m), 1084 (m), 1046 (s), 1006 (m), 989 (m), 885 (w), 804 (w), 750 (w), 732 (w), 732 (w), 668 (w), 611 (w). Thermal analysis shows a weight loss of 13.6% in the temperature range 50-220˚C, close to the calculated value for the release of five water molecules (13.3%).

Synthesis of $Cu_3(2\text{-cpp})_2(H_2O)_2$ (2). This compound was synthesized following a similar procedure to that for **1** except the reaction temperature of 140 ºC. The blue plate-like crystals were obtained in a yield of 60% (based on Cu). Elemental analysis (%) calcd. for $C_{14}H_{12}O_{12}P_2Cu_3$: C 26.91, H 1.94. Found: C 26.73, H 2.04. IR (KBr, cm^{-1}): 3447 (m), 3335 (br), 3062 (w), 1595 (w), 1580 (s), 1563 (m), 1525 (m), 1485 (m), 1441 (w), 1422 (s), 1260 (w), 1159 (w), 1132 (s), 1083 (m), 1043 (s), 978 (m), 878 (w), 799 (w), 764 (m), 726 (w), 670 (w), 612 (w). Thermal analysis shows a weight loss of 6.5% in the temperature range 150-280˚C, close to the calculated value for the release of two coordinated water molecules (5.8%).

Synthesis of $Cu_3(2\text{-cpp})_2$ (3). Compound **3** was prepared by thermal treatment of compound **1** at 240 ºC for 1 hour. Elemental analysis (%) calcd. for $C_{14}H_8O_{10}P_2Cu_3$ (**3**): C 28.56, H 1.37. Found: C 28.39, H 1.19. IR (KBr, cm^{-1}): 3440 (br), 3063 (w), 1593 (w), 1577 (s), 1542 (s), 1477 (w), 1441 (w), 1408 (m), 1259 (m), 1141 (s), 1122 (s), 1084 (s), 1043 (s), 955 (m), 881 (w), 810 (w), 754 (m), 706 (w), 662 (w), 609 (w).

Crystallographic studies. Single crystals with the sizes of 0.10 × 0.04 × 0.04 mm^3 for **1** and 0.20 × 0.20 × 0.05 mm^3 for **2** were used for structural determinations on a Bruker SMART APEX II and D8 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 296 K and 123 K, respectively. The numbers of collected and observed independent [$I > 2\sigma(I)$] reflections are 8292 and 4645 (R_{int} = 0.027) for **1** and 9533 and 1364 (R_{int} = 0.074) for **2**. The data were integrated using the Siemens SAINT program.[3] Empirical absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[4] All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms except those attaching to water molecules were put in calculated positions. The H atoms of water molecules were found from the Fourier maps. All H atoms were refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. The crystallographic data for the two compounds are listed in Table S1, and selected bond lengths and angles are given in Tables S2-S3.

References

[1] I. P. Beletskaya and M. A. Kazankova, *Russian J. Org. Chem.,* 2002, **38**, 1391–1430.

[2] O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, **1993**.

[3] *SAINT, Program for Data Extraction and Reduction*, Siemens Analytical. X-ray Instruments, Madison, WI, 1994–1996.

[4] *SHELXTL (version 5.0), Reference Manual*, Siemens Industrial Automation. Analytical Instruments, Madison, WI, 1995.

Table S1. Crystallographic data for compounds **1** and **2**.

Compounds	**1**	**2**
Formula	$C_{14}H_{18}Cu_3O_{15}P_2$	$C_{14}H_{12}Cu_3O_{12}P_2$
M	678.84	624.80
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	*P*bcn
a (Å)	8.872(2)	22.650(3)
b (Å)	9.054(3)	8.8845(11)
c (Å)	13.255(4)	8.9245(11)
β (°)	102.344(6)	90
V ($Å^3$)	1040.1(5)	1795.9(4)
Z	2	4
D_c (g cm^{-3})	2.168	2.311
μ (mm^{-1})	3.272	3.768
F(000)	678	1236
R_{int}	0.027	0.074
GoF on F^2	1.00	1.00
R_1, wR_2[a] [$I>2\sigma(I)$]	0.0256, 0.0549	0.0334, 0.0721
R_1, wR_2[a] (all data)	0.0323, 0.0565	0.0494, 0.0774
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e $Å^{-3}$	0.50, -0.44	0.57, -0.45
CCDC	1823683	1823684

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (deg) for compound **1**.

Cu1-O1	1.907(4)	Cu3-O5W	1.965(4)
Cu1-O8A	1.964(4)	Cu3-O2C	1.939(3)
Cu1-O10B	2.032(4)	P1-O1	1.510(4)
Cu1-O1W	2.282(4)	P1-O2	1.523(4)
Cu1-O2W	1.954(4)	P1-O3	1.542(4)
Cu2-O3	1.906(4)	P2-O6	1.528(4)
Cu2-O4	1.936(3)	P2-O7	1.529(4)
Cu2-O6	1.937(3)	P2-O8	1.525(4)
Cu2-O3W	1.942(4)	C7-O4	1.272(6)
Cu3-O7	1.915(4)	C7-O5	1.237(5)
Cu3-O9	1.947(3)	C14-O9	1.263(6)
Cu3-O4W	2.392(4)	C14-O10	1.253(6)
O2W-Cu1-O1	169.70(16)	O3W-Cu2-O4	88.70(15)
O2W-Cu1-O1W	91.53(15)	O3W-Cu2-O6	93.09(16)
O2W-Cu1-O7A	89.90(16)	O4-Cu2-O6	177.72(16)
O2W-Cu1-O10B	87.45(16)	O4W-Cu3-O5W	105.30(15)
O1-Cu1-O1W	98.35(14)	O4W-Cu3-O7	92.74(15)
O1-Cu1-O8A	90.12(16)	O4W-Cu3-O9	88.70(14)
O1-Cu1-O10B	90.68(16)	O2C-Cu3-O4W	90.61(15)
O8A-Cu1-O10B	169.70(16)	O5W-Cu3-O7	161.78(16)
O3W-Cu1-O10B	83.92(13)	O5W-Cu3-O9	88.84(15)
O3W-Cu1-O8A	106.32(13)	O2C-Cu3-O5W	92.69(15)
O3-Cu2-O3W	173.84(16)	O7-Cu3-O9	94.24(16)
O3-Cu2-O4	95.93(16)	O2C-Cu3-O7	84.40(15)
O3-Cu2-O6	82.19(16)	O2C-Cu3-O9	178.44(16)

Symmetry transformation used to generate equivalent atoms: A: 1-x, 0.5+y, 1-z; B: x-1, y+1, z; C: x, y-1, z; D: 1-x, -0.5+y, 1-z; E: 1+x, -1+y, z; F: 2-x, 0.5+y, 1-z.

Table S3. Selected bond lengths (Å) and angles (deg) for compound **2**.

Cu1-O1	1.916(3)	Cu2-O2D	1.932(4)
Cu1-O1A	1.916(3)	Cu2-O3F	2.586(3)
Cu1-O5B	1.958(3)	P1-O1	1.516(4)
Cu1-O5C	1.958(3)	P1-O2	1.521(3)
Cu2-O1W	1.950(3)	P1-O3	1.546(3)
Cu2-O3	1.921(3)	C7-O4	1.253(6)
Cu2-O4	1.966(4)	C7-O5	1.279(6)
O1-Cu1-O1A	145.27(16)	O1W-Cu2-O3	171.44(14)
O1-Cu1-O5B	92.13(12)	O1W-Cu2-O4	89.25(13)
O1-Cu1-O5C	94.55(13)	O1W-Cu2-O2D	91.26(14)
O5B-Cu1-O5C	157.48(15)	O3-Cu2-O4	91.62(13)
O4-Cu2-O2D	174.26(14)	O3-Cu2-O2D	O1W-Cu2-O2D

Symmetry transformation used to generate equivalent atoms: A: 1-x, y, 1.5-z; B: 1-x, 1-y, 1-z; C: x, 1-y, 0.5+z; D: x, -y, -0.5+z; E: x, -y, 0.5+z; F: 1-x, y, 0.5-z; G: 1-x, -y, 1-z.

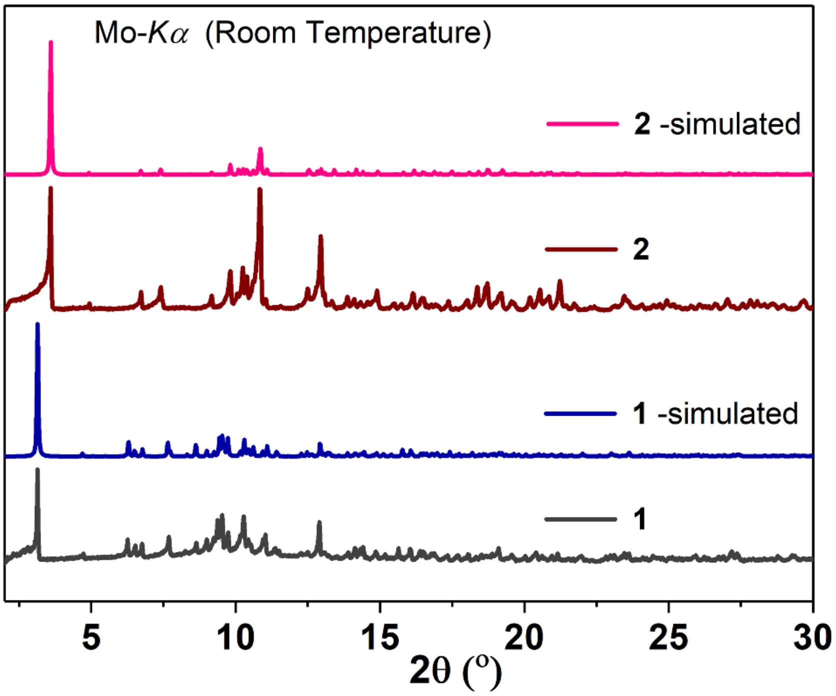


Figure S1. The PXRD patterns for compounds **1** and **2**.

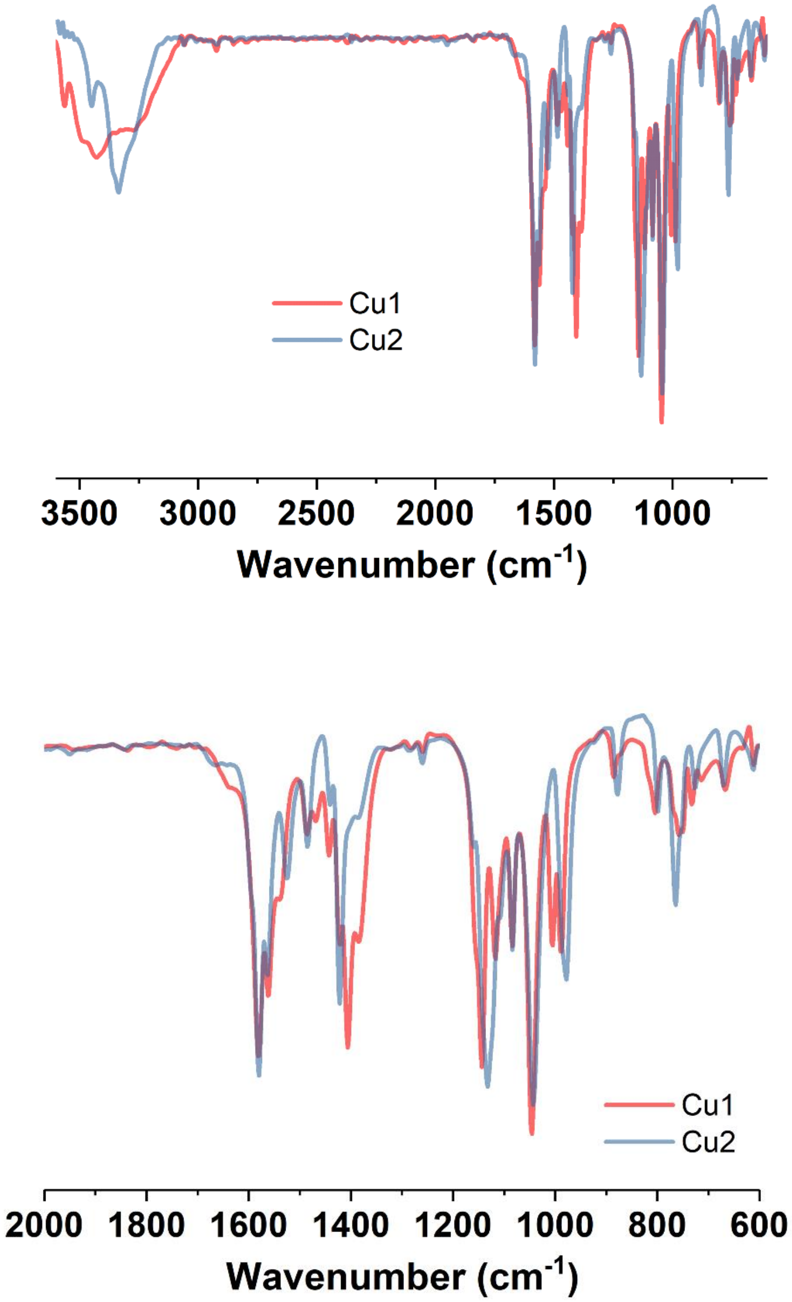


Figure S2. The IR spectra for compounds **1** and **2**.

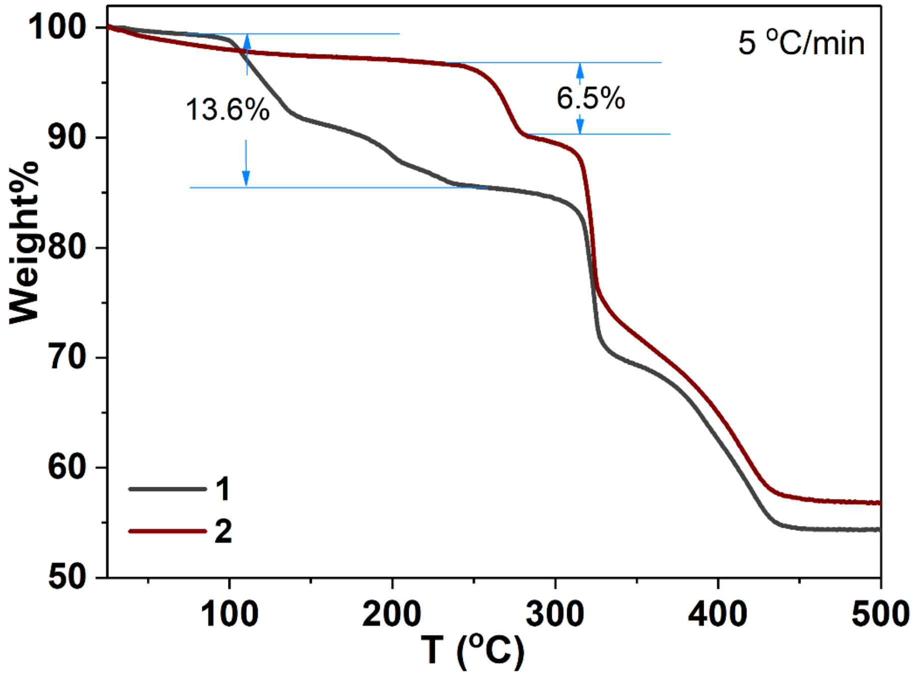


Figure S3. The TGA curves for compounds **1** and **2**.

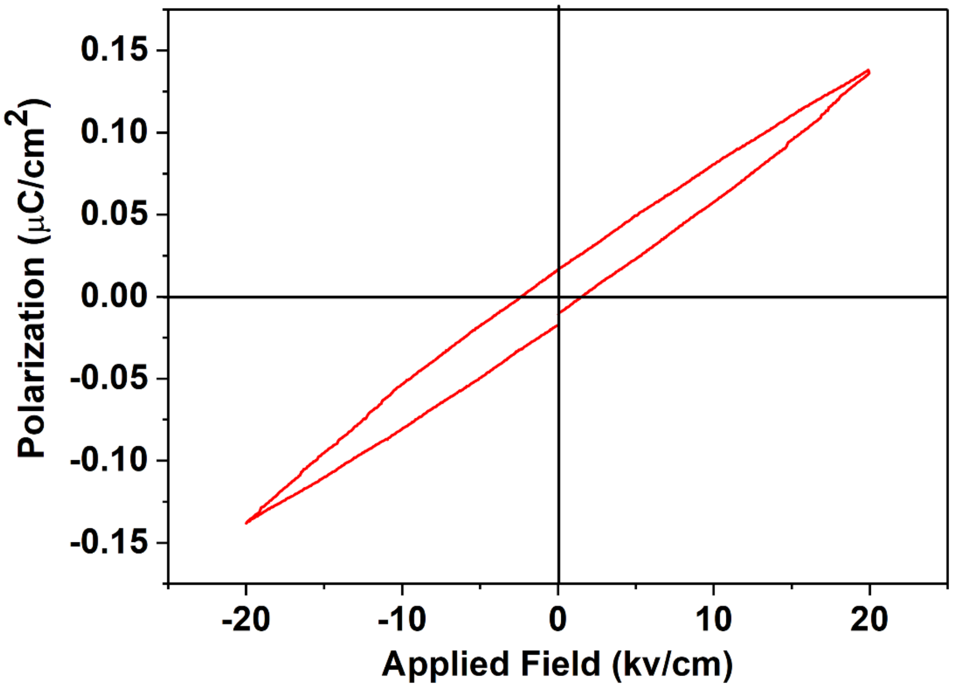


Figure S4. Electric hysteresis loop of a pellet of powder of **1** measured at room temperature.

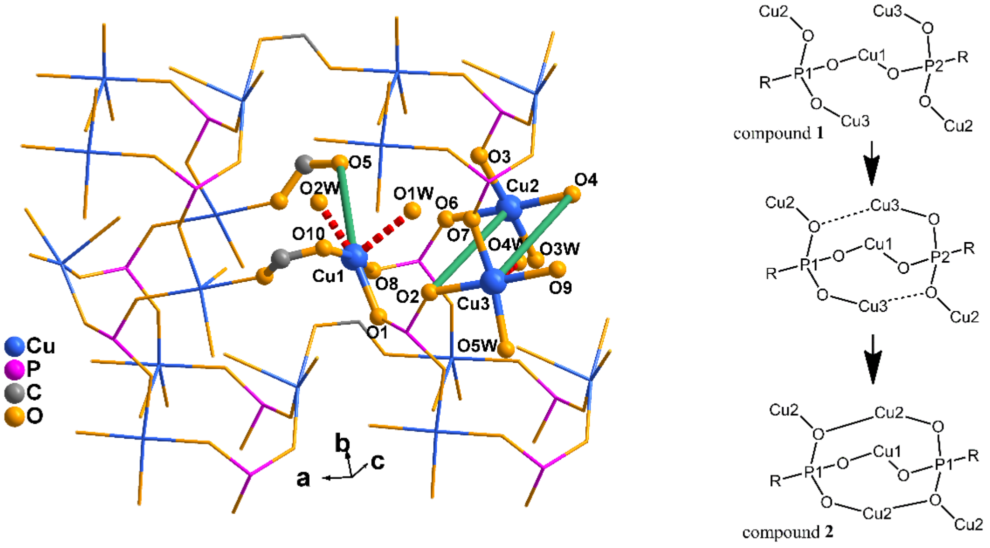


Figure S5. (a) The proposed structural transformation from **1** to **2**. The coordination water molecules (O1W, O2W, and O4W) are removed together with the breaking of the corresponding Cu-O$_{\text{water}}$ bonds (shown as the red dashed lines). The pending carboxylate oxygen (O5) and the phosphonate oxygen atoms (O2, O4) bind to Cu atoms to generate new coordination bonds (shown as the green lines). (b) A scheme to illustrate the variation of coordination modes of the phosphonate groups in **1** and **2**.

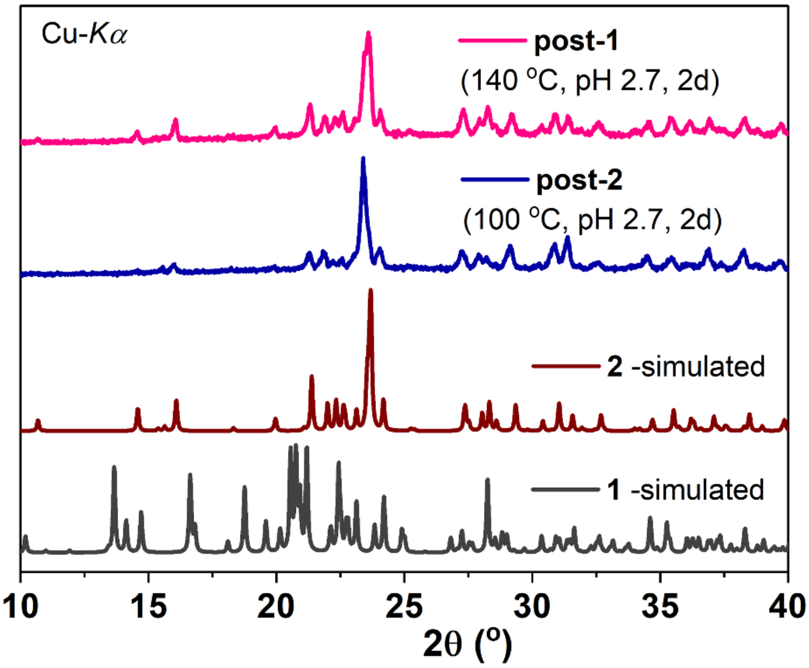


Figure S6. The PXRD patterns of the products resulted from **1** and **2** (**post-1**, **post-2**) after hydrothermal reactions (pH 2.7) at 140 °C and 100 °C, respectively. The PXRD patterns simulated from the single crystal data of compounds 1 and 2 are given for comparison.

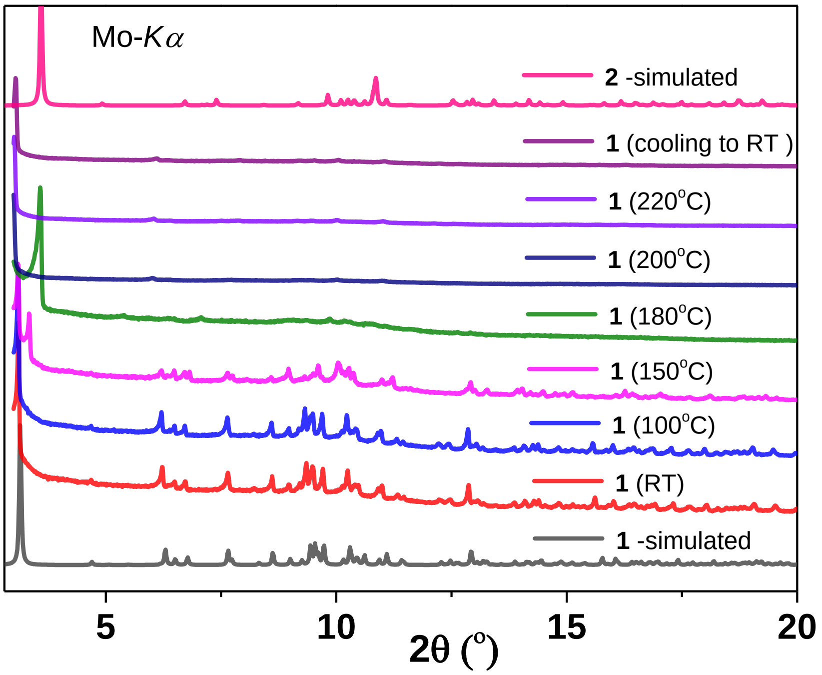
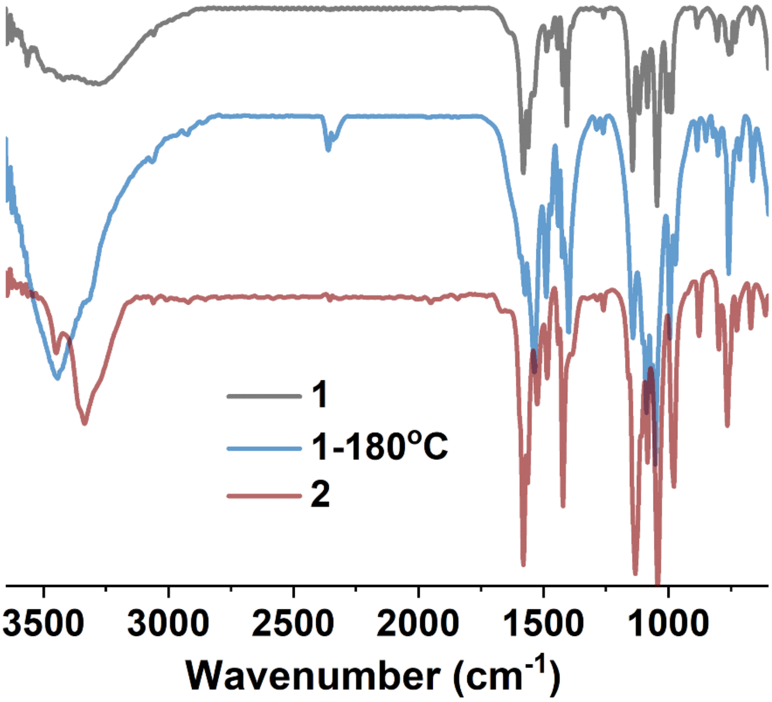


Figure S7. Variable temperature PXRD measurements of **1** in vacuum from room temperature to 220 °C. The PXRD patterns simulated from the single crystal data of compounds **1** and **2** are given for comparison.



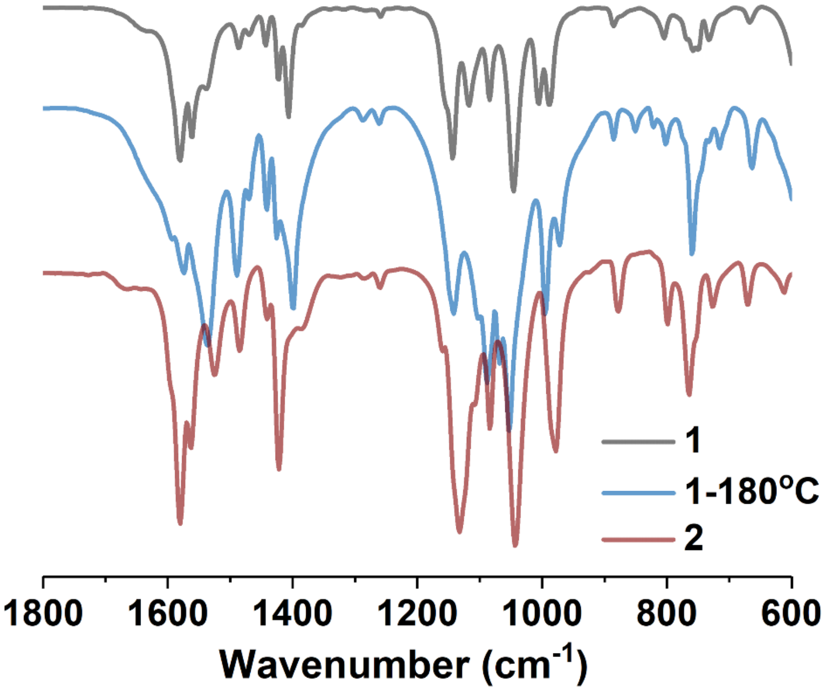


Figure S8. The IR spectra for compounds **1**, **1-180°C**, and **2**.

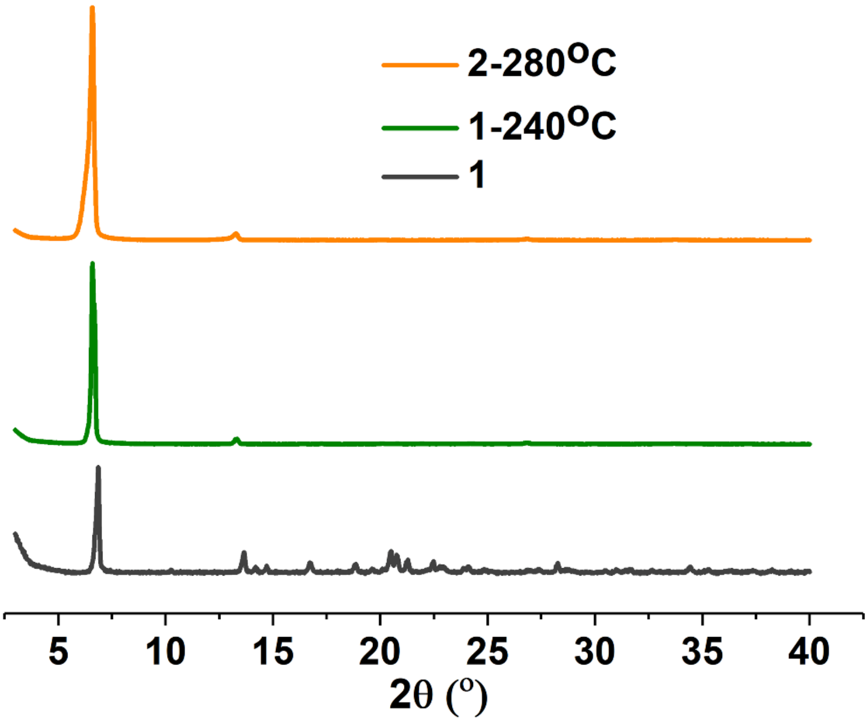
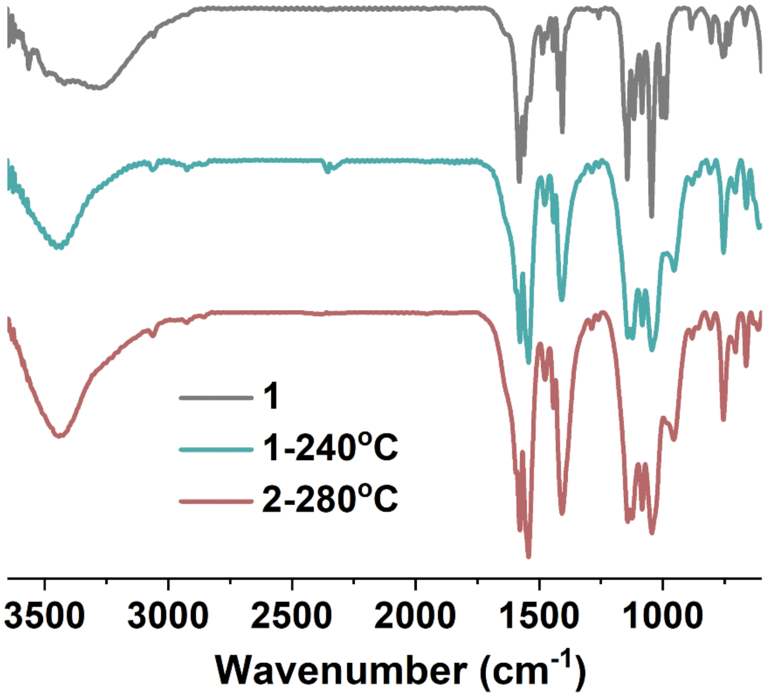


Figure S9. The PXRD patterns of **1**, **1-240°C**, and **2-280°C**.



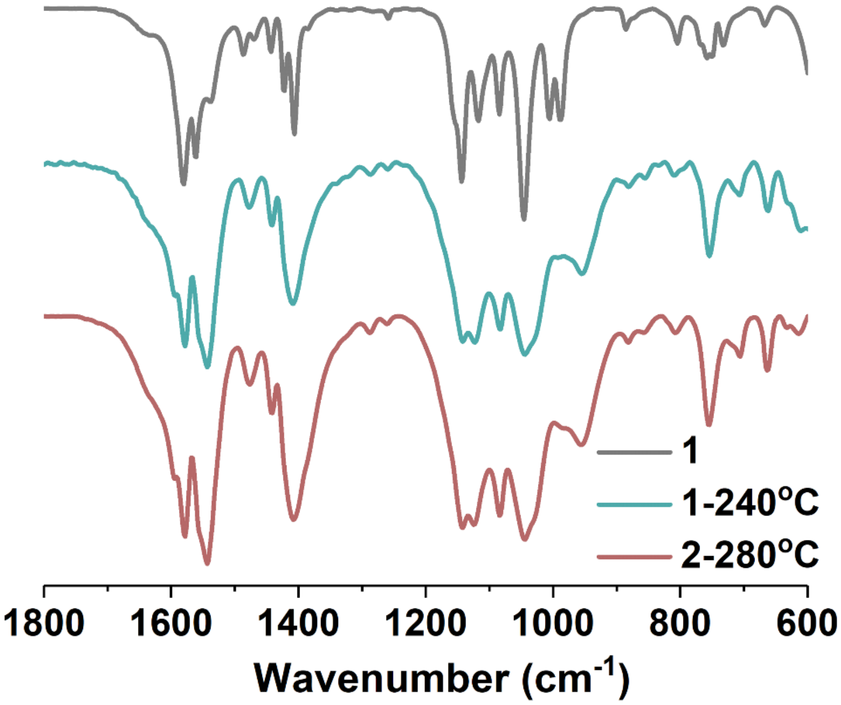


Figure S10. The IR spectra for compounds **1**, **1-240°C**, and **2-280°C**.

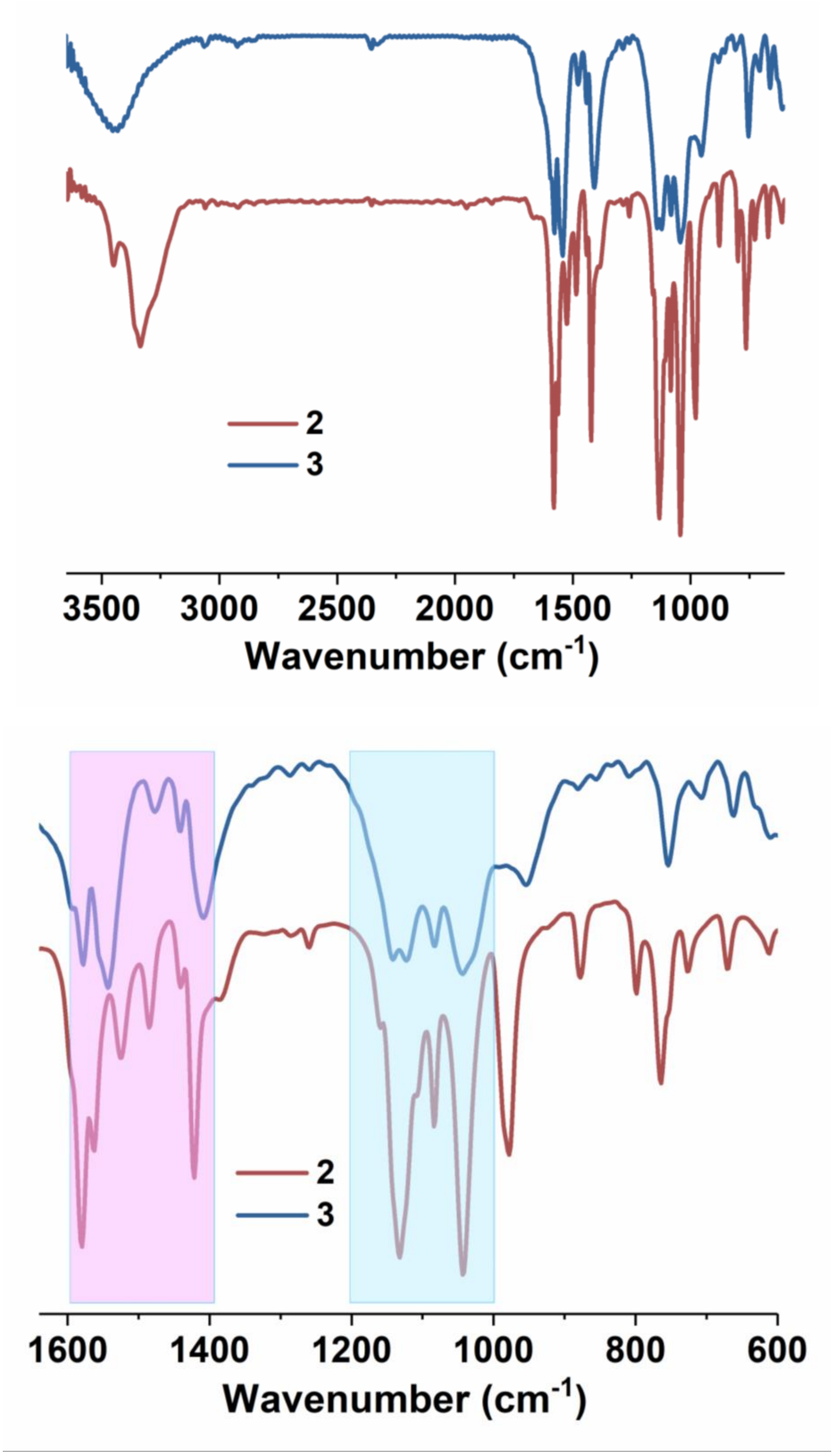


Figure S11. The IR spectra for compounds **2** and **3**.

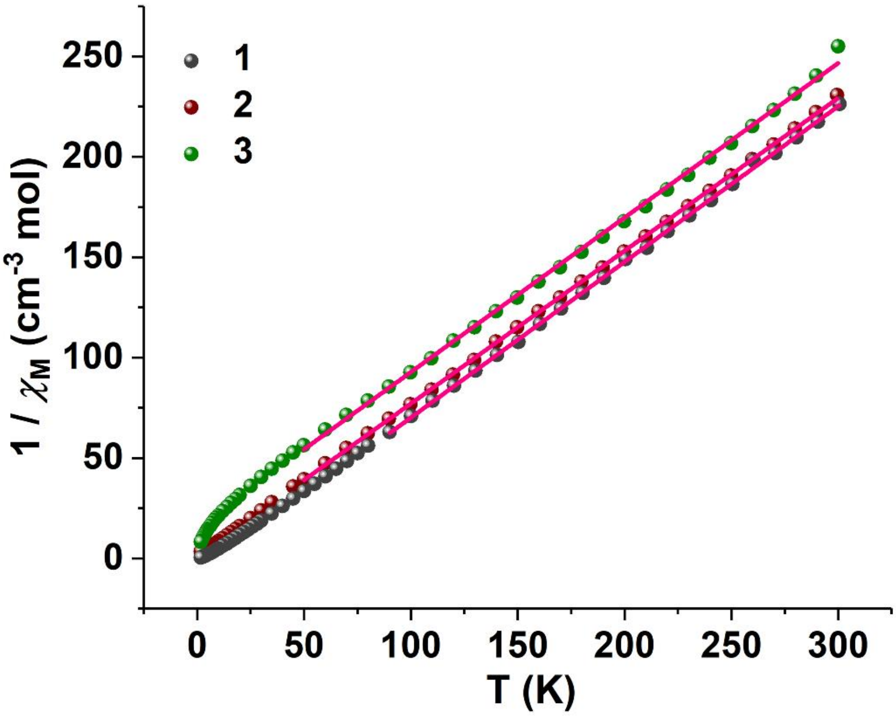


Figure S12. The 1/χ_M vs *T* plots for **1-3**. Linear fiting lines are shown in red.

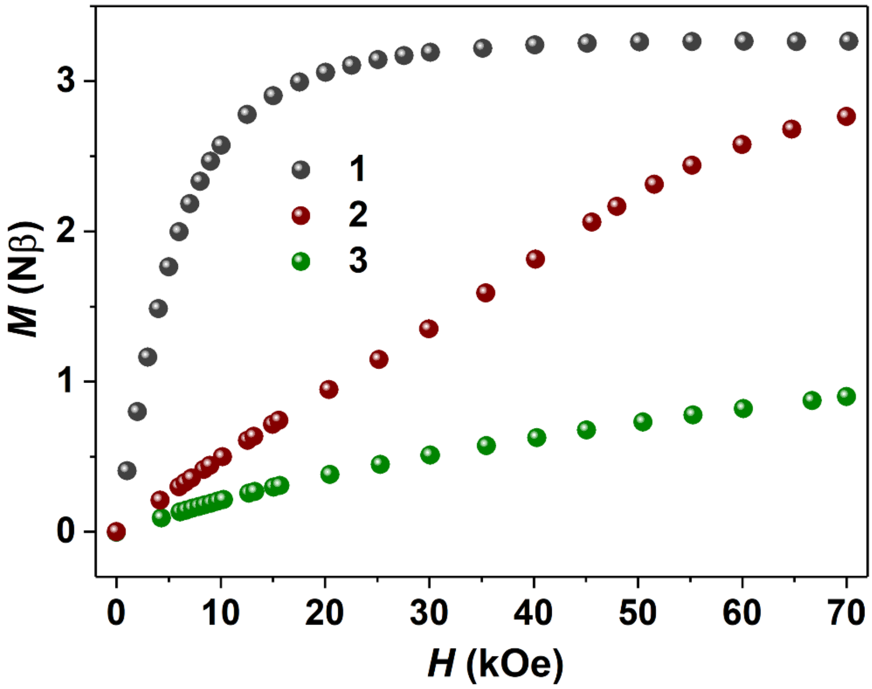


Figure S13. The field-dependent magnetization for **1-3**.