

Supporting information

Enantiopure phosphonic acids as chiral inducers: homochiral crystallization of cobalt coordination polymers showing field-induced slow magnetization relaxation

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Experimental Section

Materials and measurements. (*S*)-, (*R*)-3-phenyl-2-((phosphonomethyl)amino)propanoic acids [(*S*)-, (*R*)-2-ppapH₃] were synthesized according to the literature.¹ All other starting materials were of analytical reagent grade and used as received without further purification. Elemental analyses for C, N and H were determined with a Perkin Elmer 240C elemental analyzer. Infrared spectra were measured on a Bruker TENSOR 27 IR spectrometer with pressed KBr pellets in the range of 400-4000 cm⁻¹. Thermogravimetric analysis (TGA) were performed on a Mettler-Toledo TGA/DSC STAR^e thermal analyzer in the range of 25-600°C under a nitrogen flow at a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K) at room temperature. Magnetic measurements were performed on a Quantum Design MPMS-XL7 SQUID magnetometer. The diamagnetic contribution of the sample itself was estimated from Pascal's constants.² The circular dichroism spectra were recorded on a JASCO J-720W spectropolarimeter at room temperature. Approximate estimations of the second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powder sample (80±150 mm diameter) in the form of a pellet (Kurtz powder test³), with that obtained for urea. A pulsed Q-switched Nd: YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave

mirror and passed through a filter that transmits only 532 nm radiation.

Synthesis of *1M* and *1P*. The two compounds were synthesized under similar experimental conditions except the chiral inducing agent (*(S)*-2-ppapH₃ for *1M* and *(R)*-2-ppapH₃ for *1P*). A typical procedure for the preparation of *1M* is described as below. A mixture of CoSO₄·7H₂O (0.0562 g, 0.2 mmol), *(S)*-2-ppapH₃ (0.0026 g, 0.01 mmol) and 1,3-bbix (0.0776 g, 0.2 mmol) in 5 mL of water/methanol (3/2) was kept in a 10 mL Teflon-lined stainless container and heated at 100°C for 2 d. After being cooled to room temperature, red needle-like crystals were obtained by suction filtration, washed with a minimum amount of methanol and water, respectively. Yield: 34.2 mg (31.2% based on Co). Elemental analysis (%) calcd for C₂₂H₂₄N₄O₇SCo: C, 48.27; H, 4.42; N, 10.23. Found: C, 48.80; H, 4.65; N, 10.30. IR (KBr, cm⁻¹): 3111(s), 1612(w), 1506(m), 1462(m), 1444(m), 1386(w), 1262(w), 1196(w), 1140(s), 1092(s), 747(s), 606(m), 426(w). Same product was obtained when the amount of *(S)*-2-ppapH₃ was reduced to 0.0026 g (0.01 mmol).

For *1P*: Yield: 33.5 mg (30.6% based on Co). Elemental analysis (%) calcd for C₂₂H₂₄N₄O₇SCo: C, 48.27; H, 4.42; N, 10.23. Found: C, 48.77; H, 4.68; N, 10.23. IR (KBr, cm⁻¹): 3111(s), 1612(w), 1507(m), 1462(m), 1444(m), 1386(w), 1262(w), 1196(w), 1140(s), 1092(s), 747(s), 606(m), 426(w).

Synthesis of Con-1. A mixture of CoSO₄·7H₂O (0.0562 g, 0.2 mmol), *Rac*-2-ppapH₃ (0.0026 g, 0.01 mmol) and 1,3-bbix (0.0776 g, 0.2 mmol) in 5 mL of water/methanol(3/2) was kept in a 10 mL Teflon-lined stainless container and heated at 100°C for 2 d. After being cooled to room temperature, red needle-like crystals were obtained by suction filtration, washed with a minimum amount of methanol and water, respectively. Yield: 33.7 mg (30.8% based on Co). Elemental analysis (%) calcd for C₂₂H₂₄N₄O₇CoS: C, 48.27; H, 4.42; N, 10.23. Found: C, 48.55; H, 4.56; N, 10.27. IR (KBr, cm⁻¹): 3111(s), 1612(w), 1507(m), 1462(m), 1444(m), 1386(w), 1262(w), 1195(w), 1140(s), 1092(s), 747(s), 606(m), 426(w).

Synthesis of Con-2. A mixture of CoSO₄·7H₂O (0.0562 g, 0.2 mmol) and 1,3-bbix (0.0776 g, 0.2 mmol) in 5 mL of water was kept in a 10 mL Teflon-lined stainless container and heated at 100°C for 2 d. After being cooled to room

temperature, red needle-like crystals were obtained by suction filtration, washed with a minimum amount of methanol and water, respectively. Yield: 31.0 mg (28.3% based on Co). Elemental analysis (%) calcd for C₂₂H₂₄N₄O₇CoS: C, 48.27; H, 4.42; N, 10.23. Found: C, 48.13; H, 4.49; N, 10.26. IR (KBr, cm⁻¹): 3112(s), 1612(w), 1507(m), 1463(m), 1444(m), 1386(w), 1262(w), 1195(w), 1140(s), 1093(s), 747(s), 606(m), 427(w).

Crystallographic studies. Single crystals with dimensions 0.2×0.1×0.05 mm³ for **1M** and 0.3×0.1×0.1 mm³ for **1P** were used for structural determination on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K α (λ = 0.71073 Å) radiation at 123 K for **1M**, 296 K for **1P**. A hemisphere of data was collected in the θ range of 1.83-27.69° for **1M**, and 1.82-27.52° for **1P** using an exposure time of 25 s per frame for **1M** and 5 s for **1P**. The numbers of observed and unique reflections are 9857 and 4181 (R_{int} = 0.067) for **1M**, 10159 and 4539 (R_{int} = 0.091) for **1P**. The data were integrated using the Siemens *SAINTE* program⁴, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multiscan absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full matrix least squares using *SHELXTL*⁵. All the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Details of the crystal data and refinements are summarized in Table S1 for **1M** and **1P**. Selected bond lengths and angles are listed in Table S2 for **1M** and **1P**.

References

- [1] (a) H. Zhu, J. Huang, S. S. Bao, M. Ren, L. M. Zheng, *Dalton Trans.* **2013**, 42, 14075-14080; (b) J.-S. Feng, S.-S. Bao, M. Ren, Z.-S. Cai, L.-M. Zheng, *Chem. Eur. J.* **2015**, 21, 17336-17343.
- [2] O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.
- [3] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1968**, 39, 3798.

- [4] SAINT, Program for Data Extraction and Reduction, Siemens Analytical X-ray Instruments, Madison, WI, **1994–1996**.
- [5] SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments, Madison, WI, **1995**.

Table S1. Crystallographic data for compounds **1M** and **1P**.

	1M	1P
Formula	C ₂₂ H ₂₄ N ₄ O ₇ SCo	C ₂₂ H ₂₄ N ₄ O ₇ SCo
<i>M</i>	547.44	547.44
crystal size [mm]	0.2×0.1×0.05	0.3×0.1×0.1
crystal system	Monoclinic	Monoclinic
space group	<i>P2</i> ₁	<i>P2</i> ₁
<i>a</i> [Å]	11.479(4)	11.495(4)
<i>b</i> [Å]	8.356(3)	8.412(3)
<i>c</i> [Å]	12.079(4)	12.098(4)
α [°]	90	90
β [°]	104.039(5)	103.450(2)
γ [°]	90	90
<i>V</i> [Å ³]	1124.0(6)	1137.7(6)
<i>Z</i>	2	2
<i>D</i> _c [g cm ⁻³]	1.618	1.598
μ [mm ⁻¹]	0.910	0.899
<i>F</i> (000)	566	566
<i>R</i> _{int}	0.067	0.091
<i>T</i> _{max} , <i>T</i> _{min}	0.956, 0.897	0.915, 0.898
GoF on <i>F</i> ²	1.00	1.00
<i>R</i> ₁ , <i>wR</i> ₂ ^[a] [<i>I</i> > 2σ(<i>I</i>)]	0.0976, 0.2295	0.0562, 0.1264
(all data)	0.1110, 0.2384	0.0723, 0.1358
Flack parameter	0.05(4)	0.09(3)
(Δρ) _{max} , (Δρ) _{min} /e Å ⁻³	2.68, -0.96	0.62, -0.80
CCDC number	1469413	1469414

$$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$$

Table S2. Selected bond lengths (Å) and angles (°) for compounds **1M** and **1P**.

	1M	1P
Co1-O2W	2.096(6)	2.090(5)
Co1-N4A	2.114(7)	2.124(5)
Co1-O1W	2.122(6)	2.118(4)
Co1-N1	2.124(6)	2.120(5)
Co1-O3W	2.146(6)	2.153(4)
Co1-O1	2.156(6)	2.170(5)
O2W-Co1-N4A	177.5(2)	178.56(18)
O2W-Co1-O1W	93.8(2)	93.01(16)
N4A-Co1-O1W	88.7(2)	88.36(18)
O2W-Co1-N1	90.3(2)	90.93(19)
N4A-Co1-N1	87.3(3)	87.67(15)
O1W-Co1-N1	173.5(3)	173.90(19)
O2W-Co1-O3W	88.8(2)	88.74(19)
N4A-Co1-O3W	91.1(3)	91.0(2)
O1W-Co1-O3W	82.2(2)	82.17(17)
N1-Co1-O3W	103.0(2)	102.59(19)
O2W-Co1-O1	82.5(2)	81.96(19)
N4A-Co1-O1	98.0(3)	98.5(2)
O1W-Co1-O1	88.8(2)	88.52(15)
N1-Co1-O1	86.7(2)	87.42(17)
O3W-Co1-O1	167.1(2)	166.49(17)

Symmetry codes: **1M**: A: $-x+1, y-1/2, -z$; B: $-x+1, y+1/2, -z$; **1P**: A: $-x+1, y+1/2, -z+2$; B: $-x+1, y-1/2, -z+2$.

Table S3. Hydrogen bonding parameters for **1M**.

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A)(Å)	<(D-H...A) (°)
C(12)-H(12B)...O(4)#5	0.99	2.24	3.233(10)	178
C(19)-H(19)...O(1)	0.95	2.27	2.850(10)	119
C(20)-H(20)...O(3)#5	0.95	2.57	3.389(10)	145
C(22)-H(22B)...O(2)#4	0.99	2.37	3.319(10)	160
C(3)-H(3)...O(1)#1	0.95	2.42	3.181(10)	137
C(7)-H(7)...O(3W)#1	0.95	2.52	3.063(10)	116
O(1W)-H(1WA)...O(3)#3	0.85	2.33	2.828(9)	118
O(1W)-H(1WB)...O(2)	0.85	2.20	2.675(9)	115
O(2W)-H(2WA)...O(3)	0.85	2.09	2.836(9)	146
O(2W)-H(2WB)...O(2)#3	0.85	1.81	2.637(8)	165
O(3W)-H(3WA)...O(4)#2	0.85	1.96	2.653(9)	138
O(3W)-H(3WB)...O(3)#3	0.85	2.42	2.997(8)	125

Symmetry codes: **1M**: #1: -x+1, y+1/2, -z; #2: x, y-1, z; #3: -x, y-1/2, -z+1; #4: x, y, z-1; #5: -x, y-1/2, -z.

Table S4. Hydrogen bonding parameters for **1P**.

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A)(Å)	<(D-H...A) (°)
C(12)-H(12A)...O(4)#5	0.97	2.31	3.287(8)	178
C(19)-H(19)...O(1)	0.93	2.31	2.890(7)	120
C(22)-H(22A)...O(2)#4	0.97	2.41	3.338(8)	159
C(3)-H(3)...O(1)#1	0.93	2.45	3.196(10)	137
C(7)-H(7)...O(3W)#1	0.93	2.54	3.080(9)	117
O(1W)-H(1WA)...O(3)#3	0.85	2.31	2.833(7)	120
O(1W)-H(1WB)...O(2)	0.85	2.20	2.681(7)	116
O(2W)-H(2WA)...O(3)	0.85	2.08	2.836(7)	147
O(2W)-H(2WB)...O(2)#3	0.85	1.81	2.645(6)	166
O(3W)-H(3WA)...O(4)#2	0.85	1.99	2.666(7)	136
O(3W)-H(3WB)...O(3)#3	0.85	2.43	3.001(7)	124.7

Symmetry codes: **1P**: #1: -x+1, y-1/2, -z+2; #2: x, y+1, z; #3: -x+2, y+1/2, -z+1; #4: x, y, z+1; #5: -x+2, y+1/2, -z+2.

Table S5. Crystallographic data of randomly selected crystals in **1M**.

sample	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta[^\circ]$	$V(\text{\AA}^3)$	R_1	wR_2	Flack parameter
1M-1	11.475(3)	8.355(2)	12.090(3)	104.119(5)	1124.1(5)	0.0798	0.2179	0.04(3)
1M-2	11.4762(9)	8.3590(7)	12.1027(10)	104.1370(10)	1125.84(16)	0.0496	0.1170	0.019(16)
1M-3	11.469(2)	8.3515(16)	12.094(2)	104.160(3)	1123.3(4)	0.0636	0.1689	0.04(2)
1M-4	11.480(2)	8.3624(16)	12.107(2)	104.143(3)	1127.0(4)	0.0600	0.1510	0.03(2)
1M-5	11.478(2)	8.3554(17)	12.101(3)	104.181(4)	1125.1(4)	0.0716	0.1968	0.04(3)
1M-6	11.463(3)	8.350(2)	12.078(3)	104.158(4)	1121.0(5)	0.0719	0.2027	0.05(3)

Table S6. Crystallographic data of randomly selected crystals in **1P**.

sample	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta[^\circ]$	$V(\text{\AA}^3)$	R_1	wR_2	Flack parameter
1P-1	11.4772(18)	8.3611(13)	12.1024(19)	104.148(3)	1126.1(3)	0.0592	0.1605	0.04(2)
1P-2	11.4745(14)	8.3617(10)	12.1018(15)	104.129(2)	1126.0(2)	0.0500	0.1373	0.031(19)
1P-3	11.4679(18)	8.3598(13)	12.0939(18)	104.101(3)	1124.5(3)	0.0611	0.1599	0.02(2)
1P-4	11.4727(14)	8.3576(10)	12.0978(15)	104.141(2)	1124.8(2)	0.0497	0.1347	0.000(19)
1P-5	11.460(3)	8.348(2)	12.084(3)	104.154(4)	1121.0(5)	0.0756	0.2158	0.05(3)
1P-6	11.4710(10)	8.3571(7)	12.0979(10)	104.1417(13)	1124.61(16)	0.0439	0.1048	0.031(16)

Table S7. Crystallographic data of randomly selected crystals in **Con-1**.

sample	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta[^\circ]$	$V(\text{\AA}^3)$	R_1	wR_2	Flack parameter
1-1-<i>M</i>	11.4768(10)	8.3511(7)	12.0900(11)	104.1358(17)	1123.67(17)	0.0545	0.1166	-0.03(2)
1-2-<i>M</i>	11.472(2)	8.3421(16)	12.076(2)	104.117(3)	1120.8(4)	0.0566	0.1428	0.02(2)
1-3-<i>P</i>	11.475(4)	8.349(3)	12.061(4)	104.095(6)	1120.8(6)	0.0662	0.1480	0.05(3)
1-4-<i>M</i>	11.4697(16)	8.3504(11)	12.0832(16)	104.140(3)	1122.2(3)	0.0533	0.1131	0.038(19)
1-5-<i>P</i>	11.4746(14)	8.3563(10)	12.0905(14)	104.127(2)	1124.2(2)	0.0507	0.1070	0.002(18)
1-6-<i>M</i>	11.4792(10)	8.3523(7)	12.0997(11)	104.0898(14)	1125.19(17)	0.0345	0.0784	0.037(17)

Table S8. Cell parameters of compound **1M** and its dehydrated (**1M-de**) and rehydrated (**1M-de-re**) products obtained by Pawley fitting on the powder X-ray diffraction pattern using *Topas* 4.2 program.

	1M	1M-de	1M-de-re
<i>Cell</i>	$P2_1$	$P1$	$P2_1$
<i>a</i> (Å)	11.53	11.09	11.72
<i>b</i> (Å)	8.44	8.30	8.40
<i>c</i> (Å)	12.13	10.61	11.92
α (°)	90	91.0	90
β (°)	103.5	87.3	103.6
γ (°)	90	88.4	90
<i>V</i> (Å ³)	1149.3	976.0	1140.4
<i>Rwp</i>	3.21	3.87	3.57

Table S9. Cell parameters of compound **1P** and it dehydrated (**1P-de**) and rehydrated (**1P-de-re**) products obtained by Pawley fitting on the powder X-ray diffraction pattern using *Topas* 4.2 program.

	1P	1P-de	1P-de-re
<i>Cell</i>	$P2_1$	$P1$	$P2_1$
<i>a</i> (Å)	11.53	11.08	11.70
<i>b</i> (Å)	8.44	8.28	8.41
<i>c</i> (Å)	12.13	10.63	11.91
α (°)	90	90.8	90
β (°)	103.4	87.3	103.6
γ (°)	90	88.2	90
<i>V</i> (Å ³)	1148.5	973.4	1138.9
<i>Rwp</i>	2.98	3.56	3.79

Table S10. The parameters obtained by fitting the χ_M'' versus frequency data of compound **1M** under 1.5 kOe *dc* field.

T / K	$\chi_T / \text{cm}^3 \cdot \text{mol}^{-1}$	$\chi_S / \text{cm}^3 \cdot \text{mol}^{-1}$	$\ln(\tau / \text{s})$	α	R^a
1.8	1.05	0.069	-6.36	0.231	1.4×10^{-3}
2	0.95	0.059	-6.57	0.236	1.7×10^{-3}
2.2	0.88	0.053	-6.77	0.230	9.4×10^{-4}
2.4	0.82	0.050	-6.95	0.223	7.4×10^{-4}
2.6	0.77	0.048	-7.13	0.215	5.9×10^{-4}
2.8	0.72	0.051	-7.30	0.196	3.5×10^{-4}
3	0.67	0.055	-7.48	0.173	2.2×10^{-4}
3.2	0.63	0.057	-7.64	0.160	1.7×10^{-4}
3.4	0.60	0.055	-7.80	0.160	2.8×10^{-4}
3.6	0.57	0.057	-7.95	0.146	7.6×10^{-5}
3.8	0.54	0.056	-8.11	0.141	6.2×10^{-5}
4	0.52	0.060	-8.27	0.127	5.3×10^{-5}
4.2	0.50	0.062	-8.41	0.120	6.7×10^{-5}
4.4	0.47	0.063	-8.57	0.114	4.4×10^{-5}
4.6	0.45	0.066	-8.72	0.102	5.2×10^{-5}
4.8	0.44	0.071	-8.87	0.901	4.5×10^{-5}
5	0.42	0.072	-9.03	0.793	4.4×10^{-5}

$$^a R = \frac{\sum[(\chi'_{obs} - \chi'_{cal})^2 + (\chi''_{obs} - \chi''_{cal})^2]}{\sum[\chi'^2_{obs} + \chi''^2_{obs}]}$$

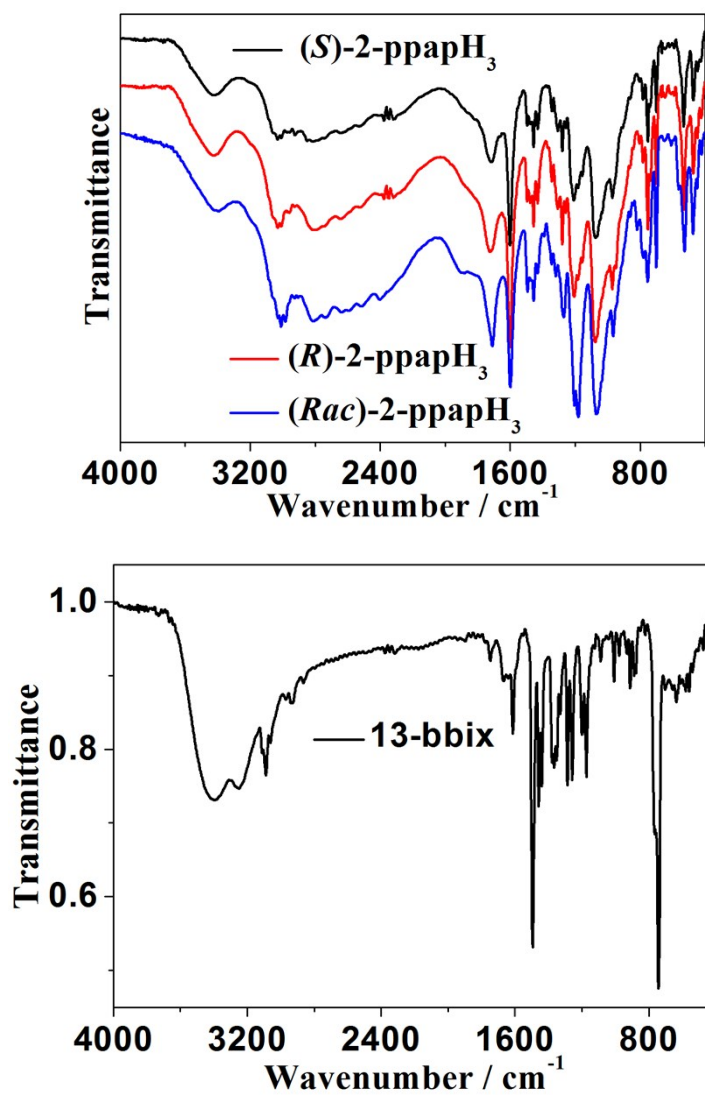


Fig. S1 The IR spectra for compounds (*S*)-2-ppapH₃, (*R*)-2-ppapH₃, *Rac*-2-ppapH₃ and 1,3-bbix.

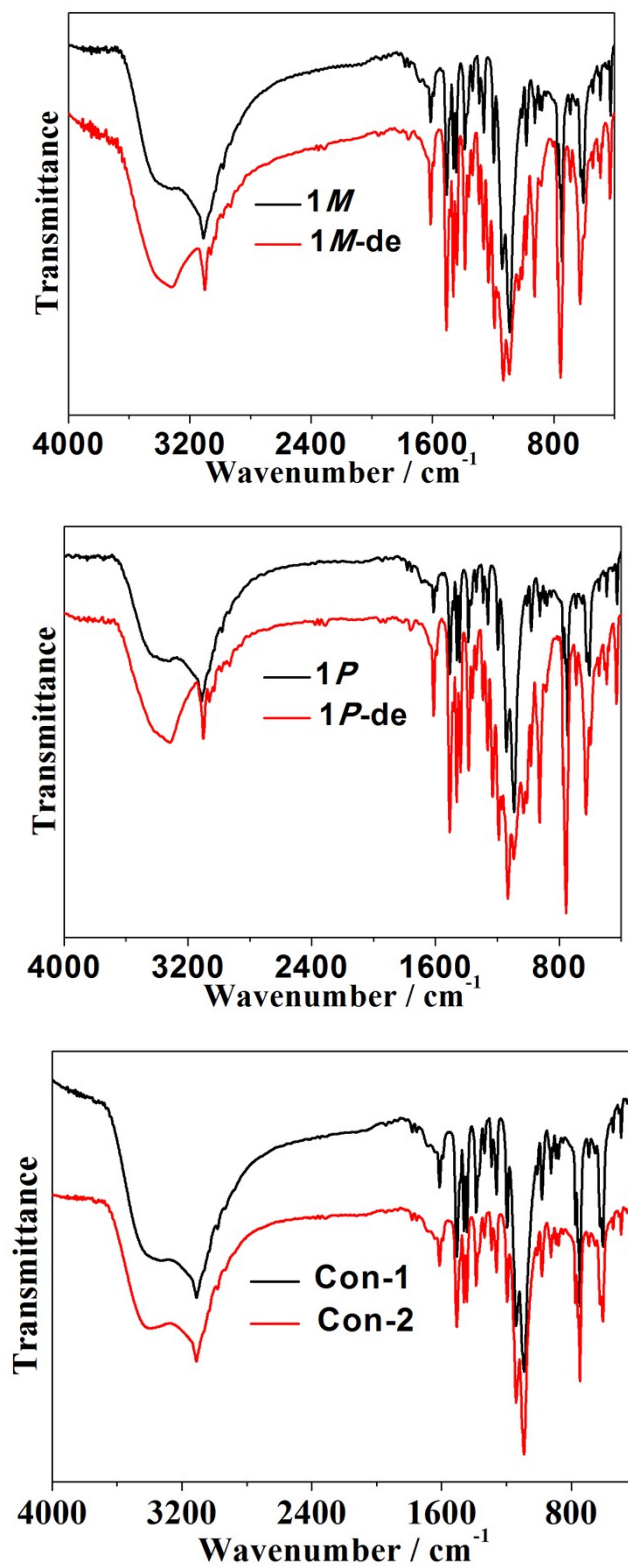


Fig. S2 The IR spectra for compounds **1M**, **1M-de**, **1P**, **1P-de**, **Con-1** and **Con-2**.

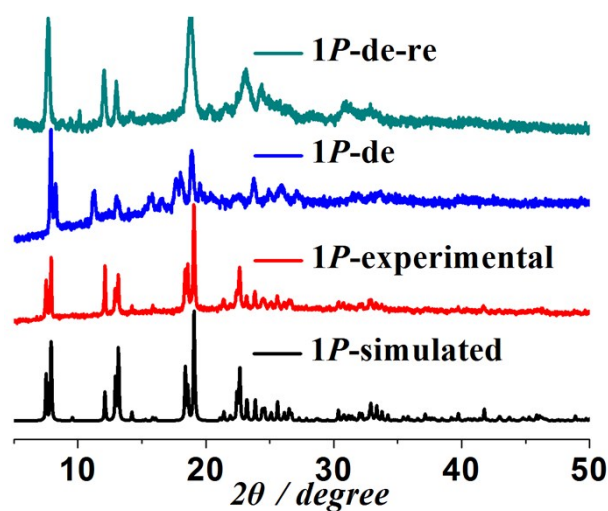
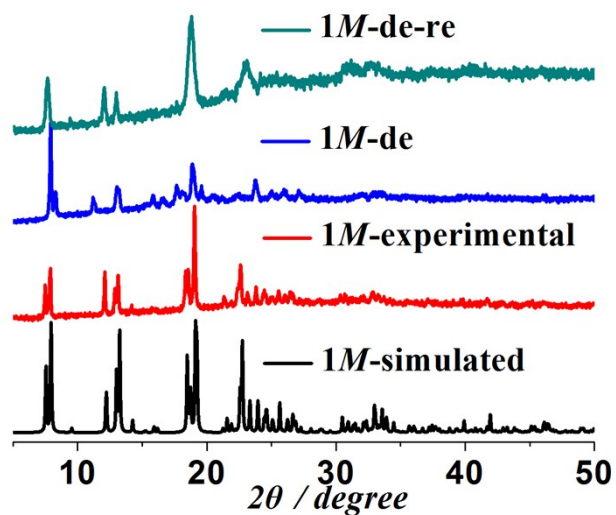


Fig. S3 PXRD patterns for compounds **1M** and **1P**, their dehydrated products (**1M-de**, **1P-de**) and re-hydrated products (**1M-de-re**, **1P-de-re**). The PXRD patterns simulated from single crystal data are also provided for comparison.

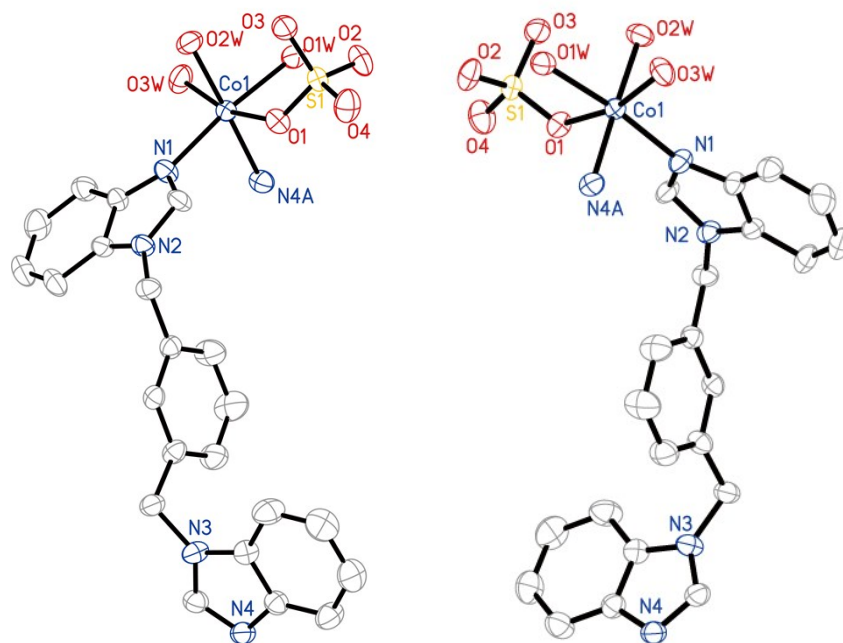


Fig. S4 Building unit of **1M** (left) and **1P** (right) showing the atomic labeling scheme (50% probability). All hydrogen atoms are omitted for clarity.

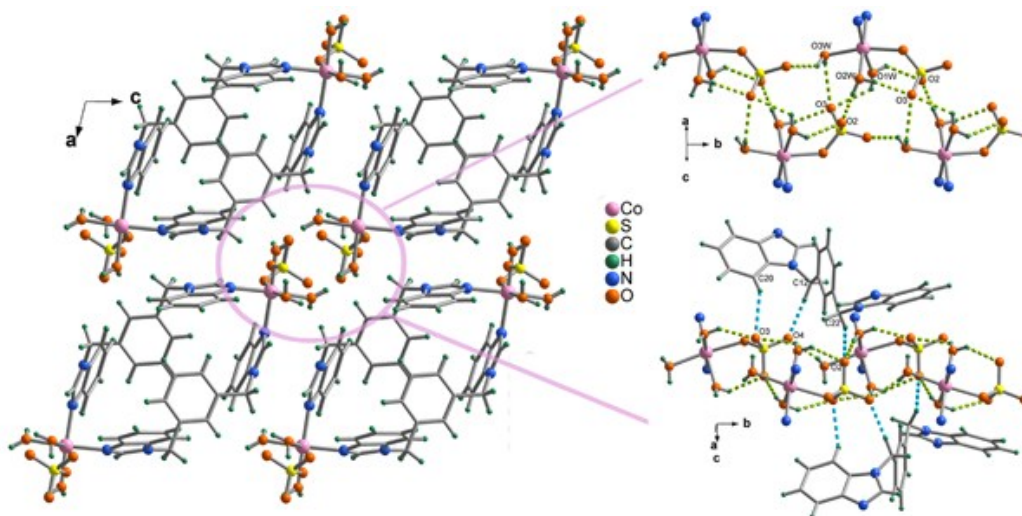


Fig. S5 The hydrogen bonding network of structure **1M**.

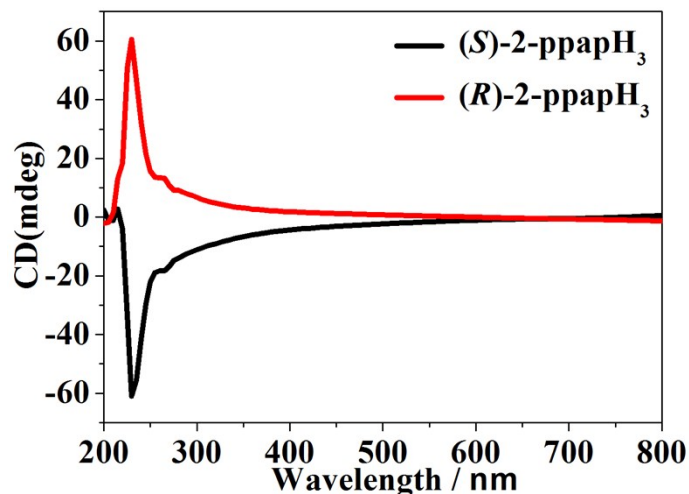


Fig. S6 The solid state CD spectra for (*S*)-2-ppapH₃ (black) and (*R*)-2-ppapH₃ (red).

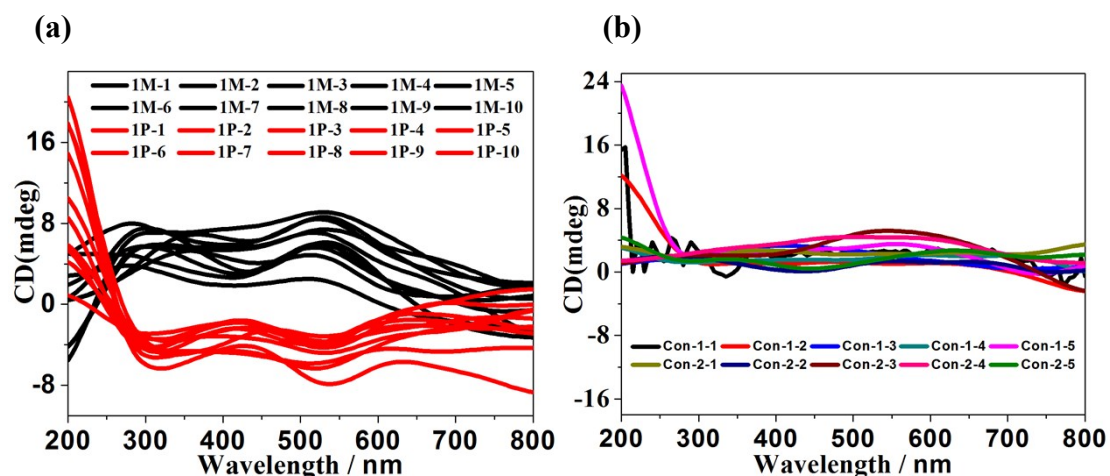


Fig. S7 (a) The solid state CD spectra for compounds **1M** and **1P**. Five samples were randomly picked from the same batch (no. 1~5) and another five samples were randomly picked from five parallel batches (no. 6~10). (b) The solid state CD spectra for **Con-1** and **Con-2**. Five samples were randomly picked from the same batch (no. 1~5)

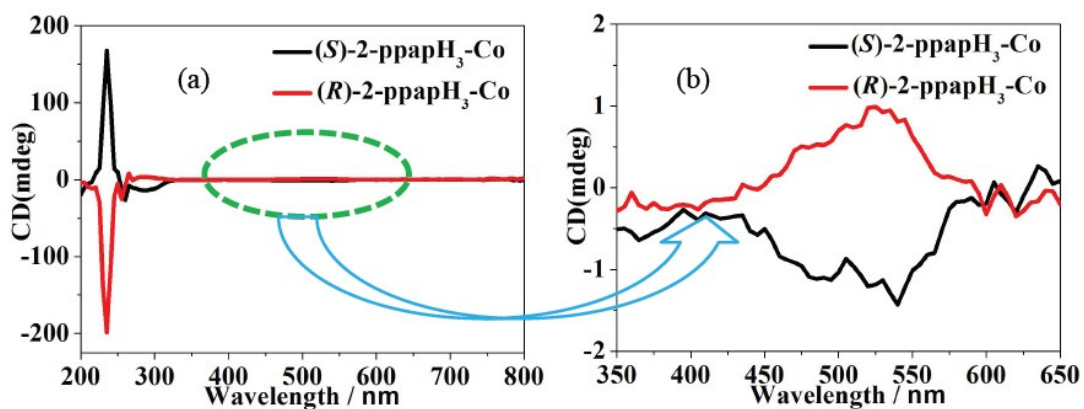


Fig. S8 Solution circular dichroism spectra for reaction mixtures of cobalt sulfate and (*S*)-2-ppapH₃ or (*R*)-2-ppapH₃ without 1,3-bbix for 1 d.

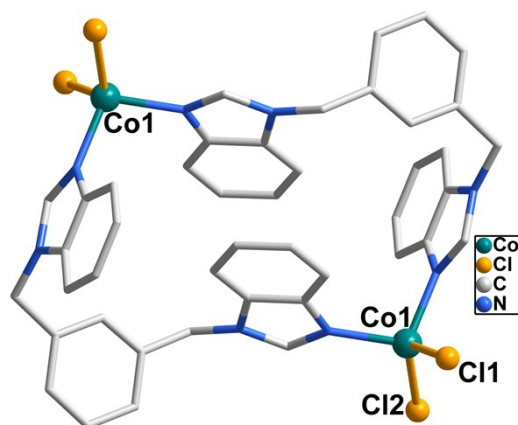


Fig. S9 Dinuclear structure of compound CoCl₂(1,3-bbix).

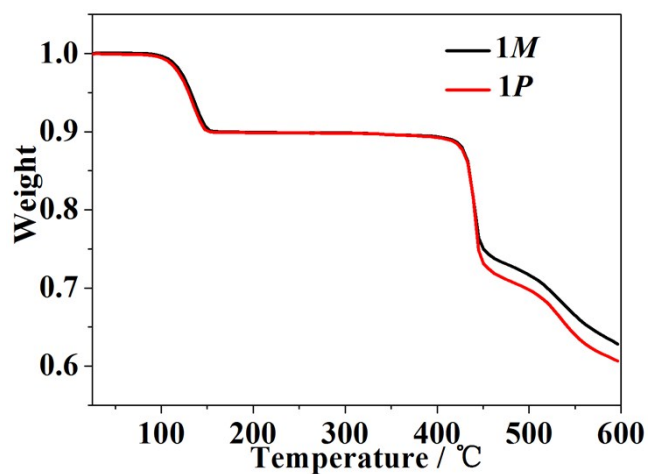


Fig. S10 TGA curves for compounds **1M** and **1P**.

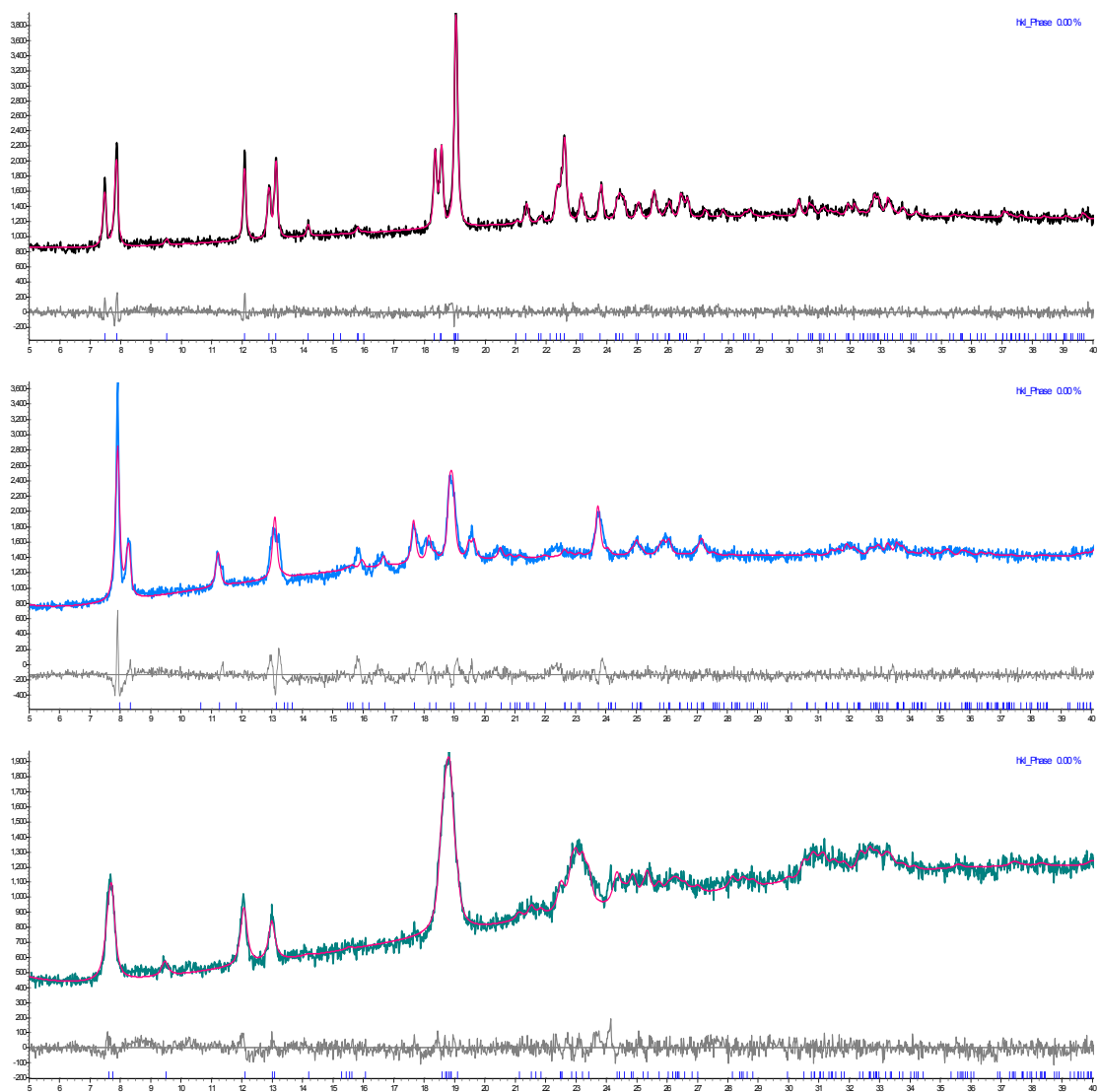


Fig. S11 Pawley fit of a powder sample of **1M** (top), **1M-de** (middle) and **1M-de-re** (bottom) performed using *Topas* 4.2 program.

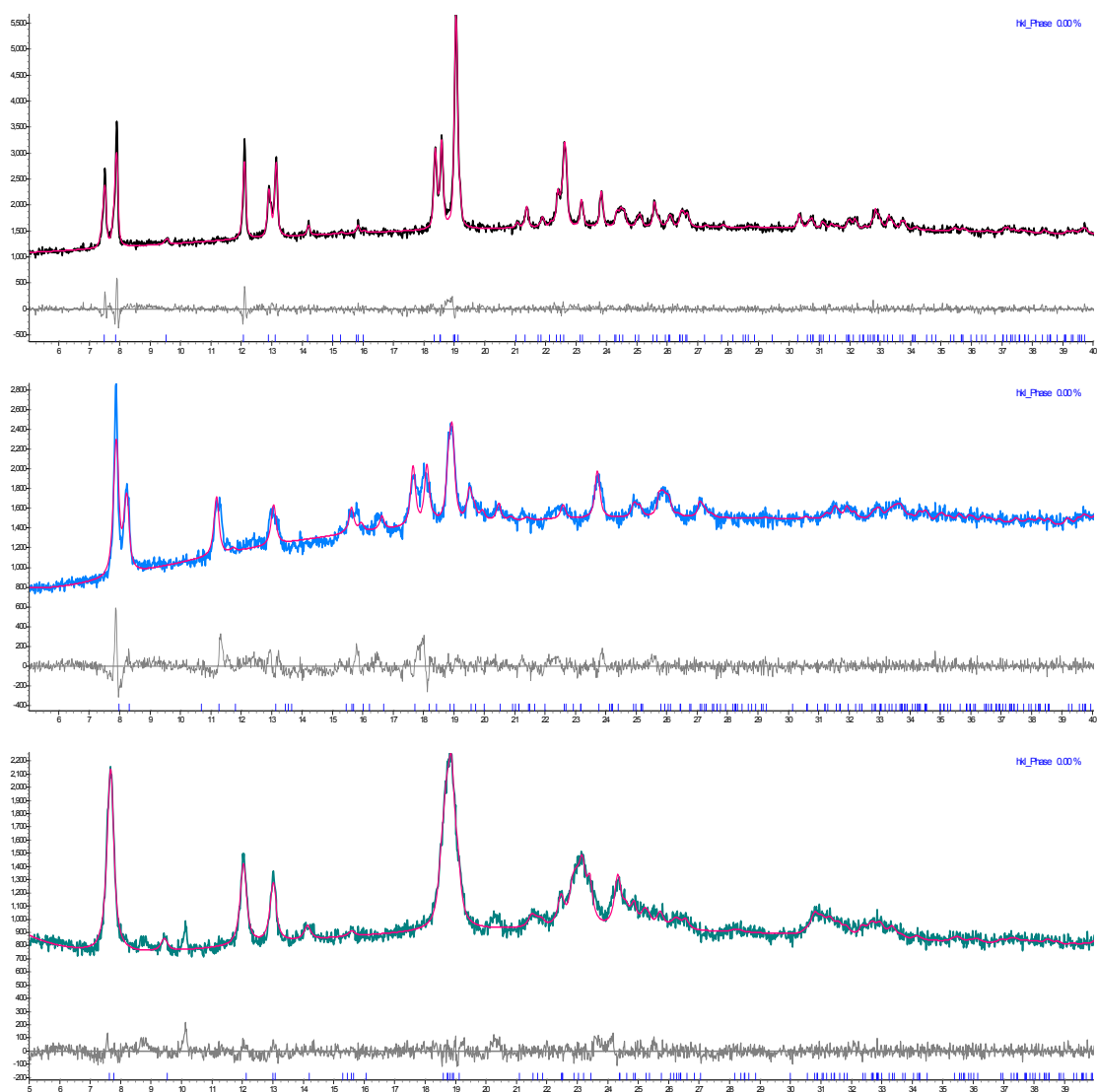


Fig. S12 Pawley fit of a powder sample of **1P** (top), **1P-de** (middle) and **1P-de-re** (bottom) performed using *Topas* 4.2 program.

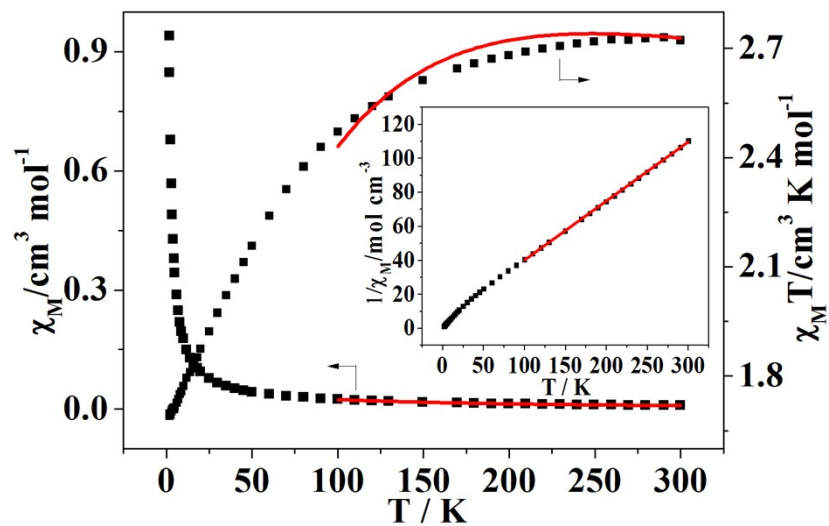


Fig. S13 The χ_M , $\chi_M T$ and $1/\chi_M$ (inset) vs. T plots for compound **1M**. The solid red lines are best fits.

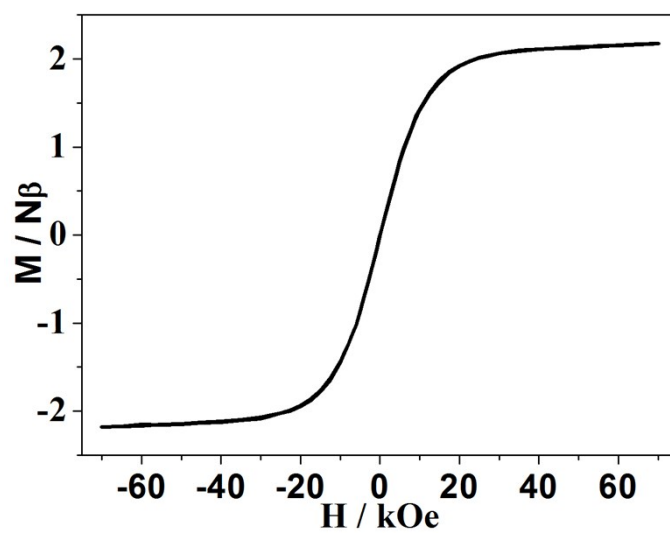


Fig. S14 The M versus H plot for compound **1M**.

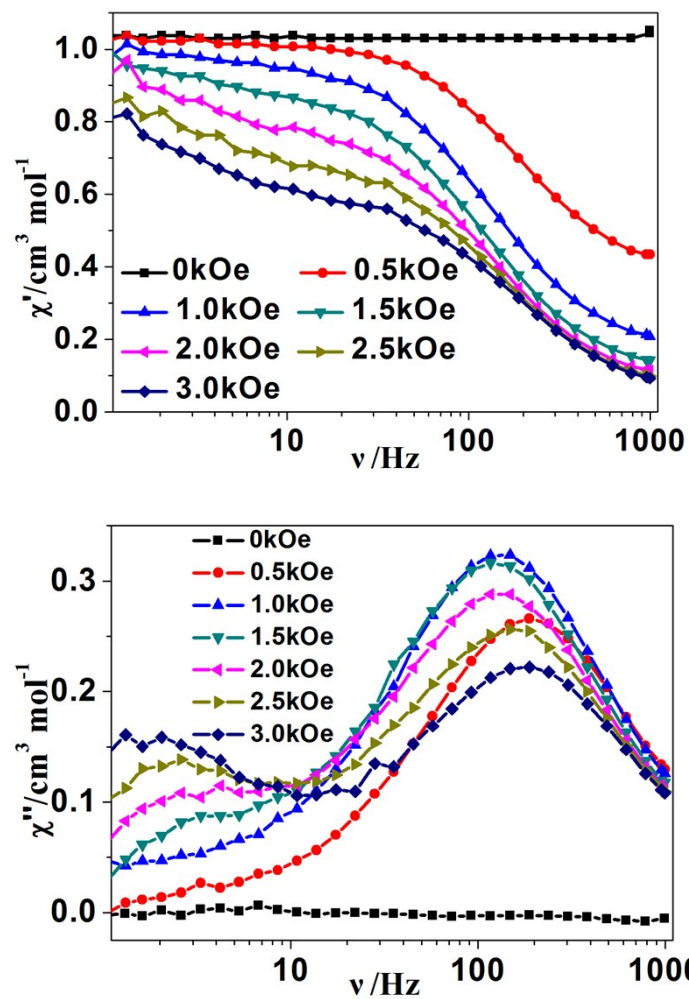


Fig. S15 Frequency dependence of the in-phase (χ_M') and out-of-phase (χ_M'') susceptibilities of **1M** at 2.0 K under different fields.

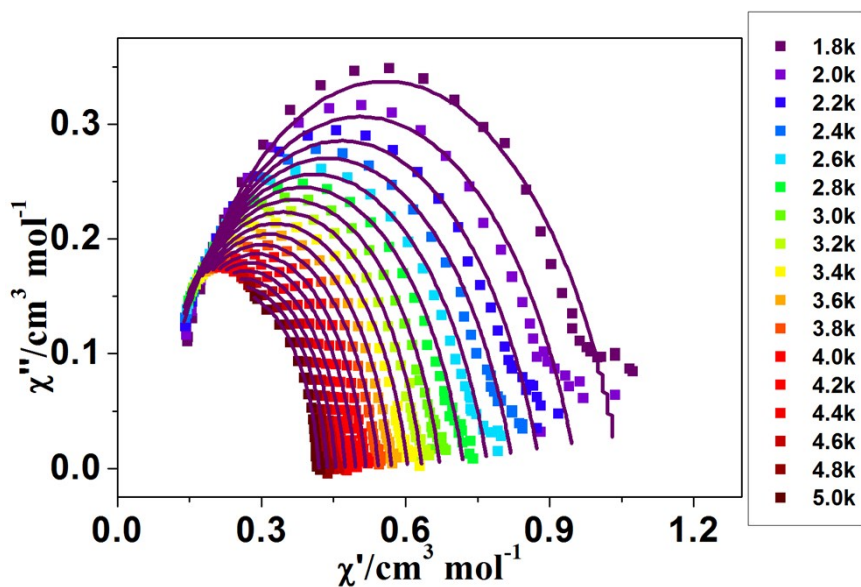


Fig. S16 The Cole-Cole plots for **1M**. The solid lines are best fits to the generalized Debye model.

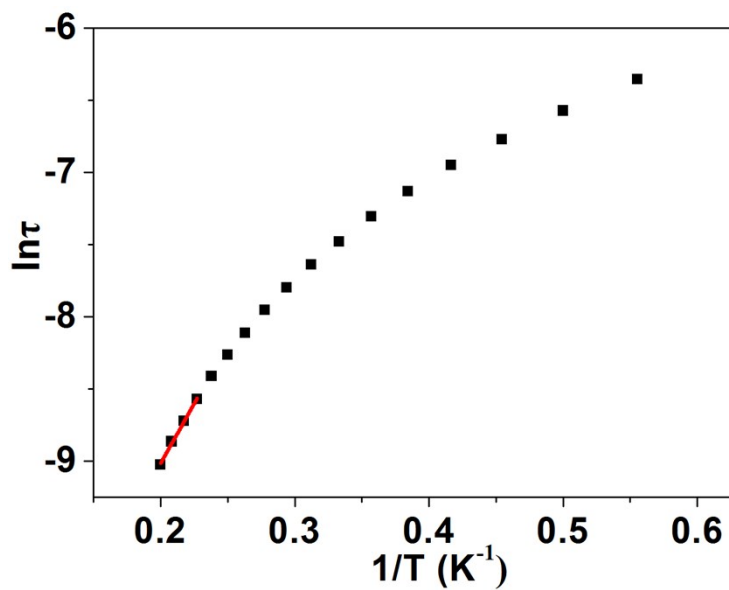


Fig. S17 Plot of $\ln(\tau)$ versus T^{-1} for **1M**. The red line represents the best fit to the Arrhenius law.

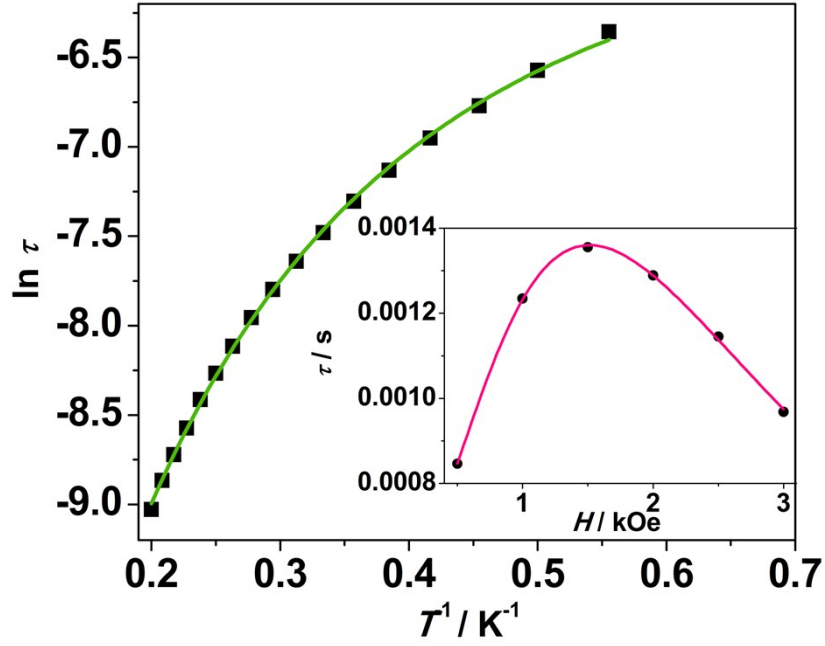


Fig. S18 The $\ln \tau$ vs. T^{-1} plot for **1M**. Inset: the τ vs. H at 2.0 K. The green line is the best fit by equ. (1), leading to parameters $U_{\text{eff}} = 31.5$ K ($\tau_0 = 6.5 \times 10^{-6}$ s) and $n = 3.5$. The red line is the best fit by $\tau^{-1} = AH^2T + B_1/(1+B_2H^2)$. The obtained A , B_1 and B_2 values are used in the data fitting by equ. (1).

$$\tau^{-1} = AH^2T + \frac{B_1}{1 + B_2H^2} + CT^n + \tau_0^{-1} \exp(-U_{\text{eff}}/kT) \quad (1)$$

where A , B_1 , B_2 , C , and n are coefficients, H is the magnetic field, T is the temperature, U_{eff} is the thermal barrier of Orbach relaxation process, τ_0 is the attempt time, and k is the Boltzmann constant.