

Electronic Supporting Information

Restraining the Motion of Ligand for Modulating the Structural Phase Transition in Two Isomorphous Polar Coordination Polymers†

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Table of contents	Page number
Materials and general methods	S2
Synthesis of [Cu(NCS) ₂](4-APy) ₂] _n (1) and [Cu(NCS) ₂](4-MeAPy) ₂] _n (2)	S2
Crystallographic Studies	S2
Table S1. Crystal data and structure refinement parameters for 1 and 2	S3
Table S2. Selected bond distances (Å) and angles (deg) for 1 and 2	S4
Table S3. Interchain hydrogen-bonds geometry (Å, deg) for 1 and 2	S4
Table S4. Selected structural parameters (Å, deg) of NCS ⁻ groups	S4
Fig. S1 Powder X-ray diffraction (PXRD) patterns of 1 at room temperature	S5
Fig. S2 Powder X-ray diffraction (PXRD) patterns of 2 at room temperature	S5
Fig. S3. The FT-IR spectra of 1 at room temperature	S6
Fig. S4. The FT-IR spectra of 2 at room temperature	S6
Fig. S5. The herringbone array of 4-APy ligands in the [Cu(NCS) ₂](4-APy)] _n chain of 1α	S7
Fig. S6. TG profiles of 1 and 2	S7
Fig. S7 The symmetry breaking process of 1 from the 1α to 1β	S8
Fig. S8 DSC profile of 1 in a heating-cooling cycle	S8
Fig. S9 The variable-temperature powder XRD patterns of 1	S9
Fig. S10. The coordination environments of Cu ²⁺ ion, [Cu(NCS) ₂](4-MeAPy)] _n chain and crystal packing of 2	S10
Fig. S11. DSC profile of 2 in a heating-cooling cycle	S10

Materials and general methods

Commercially available reagents were used as received without further purification. Infrared spectra were recorded with a Bruker TENSOR 27 Fourier transform FTIR spectrophotometer on KBr pellets in the range of 4000-400 cm^{-1} . Elemental (C, H, N and S) analyses were performed on a Perkin-Elmer Vario EL elemental analyzer with as-synthesized samples. Thermogravimetry (TG) analyses were performed on a TA Instruments TGA Q50 thermogravimetric analyzer in flowing N_2 with a heating rate of 10 K/min. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer with $\text{Cu K}\alpha$ radiation. DSC measurements were performed in heating and cooling mode in the temperature range 200-373 K on TA Q2000 DSC instrument. The measurements were carried out under nitrogen at atmospheric pressure in aluminum crucibles with a heating rate of 10 K/min.

Synthesis

[Cu(NCS)₂](4-apy)₂]_n (1**):** The $\text{Cu}(\text{SCN})_2$ methanol solution was first prepared by the reaction of stoichiometric amounts of KSCN (97.1 mg, 1 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (124.8 mg, 0.5 mmol) in methanol, followed by filtration of K_2SO_4 precipitate. Then, to the filtrate a methanol solution (10 mL) of 4-amino-pyridine (94.1 mg, 1 mmol) was added, the result mixture was stirred at room temperature for 30 minutes. After little insoluble precipitate was removed by filtration, the green solution was left undisturbed. The light green block crystals of **1** were obtained after about one week. Yield: 307.8 mg (84.0%). Elemental Analysis (%) for $\text{C}_{12}\text{H}_{12}\text{CuN}_6\text{S}_2$ (367.00) calcd: C, 39.17; H, 3.29; N, 22.84; S, 17.43; found: C, 39.40, H, 3.31, N, 23.22, S, 16.95. Infrared Spectroscopy (IR) of **1** are shown in Fig. S3.

[Cu(NCS)₂](4-MeAPy)₂]_n (2**):** This compound was prepared in a similar procedure as **1**, by using 4-methylamino-pyridine (108.1 mg, 1 mmol) in place of 4-amino-pyridine. The resulting light green crystalline product of **2** was obtained in yield of 85%. Elemental Analysis (%) for $\text{C}_{14}\text{H}_{16}\text{CuN}_6\text{S}_2$ (395.03) calcd: C, 42.46; H, 4.07; N, 21.22; S, 16.19. Found: C, 41.88; H, 4.00; N, 21.12, S, 15.99. X-ray powder diffraction and Infrared Spectroscopy (IR) of **2** are shown in Fig. S2 and Fig. S4.

Crystallographic Studies

All diffraction data of **1** were collected on a Bruker Smart Apex CCD single-crystal diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction data of **2** at 103 K were collected with an Rigaku XtaLAB P300DS single-crystal diffractometer by using graphite monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), the diffraction data of **2** at 353 K were collected on Rigaku R-Axis SPiDe IP single-crystal diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied by using multiscan program SADABS,¹ REQAB², ABSCOR³ respectively. Using Olex2 program⁴, all the structures were solved with the XS⁵ structure solution program using Direct Methods and refined with the XL⁶ refinement package using least-squares technique based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the amino groups were located from difference-Fourier maps and refined with isotropic temperature factors, constraints (dfix, himp) was used for amino groups in the refinement for high-temperature phase of **1**. The other hydrogen atoms of organic ligands were generated by the riding mode. The crystal

data and structure refinement results for these compounds are listed in Table S1. Selected bond distances and bond angles are listed in Table S2.

Table S1. Crystal data and structure refinement parameters for **1** and **2**

compounds	1		2	
	[Cu(NCS) ₂](4-APy) ₂] _n		[Cu(NCS) ₂](4-MeAPy) ₂] _n	
formula	C ₁₂ H ₁₂ CuN ₆ S ₂		C ₁₄ H ₁₆ CuN ₆ S ₂	
formula weight	367.94		395.99	
temperature (K)	103(2)	353(2)	103(2)	353(2)
crystal system	orthorhombic			
space group	<i>Pbn</i> 2 ₁	<i>Cmc</i> 2 ₁	<i>Cmc</i> 2 ₁	<i>Cmc</i> 2 ₁
<i>a</i> (Å)	15.637(1)	15.835(2)	17.930(6)	18.071(2)
<i>b</i> (Å)	15.632(1)	15.794(2)	14.618(4)	15.131(1)
<i>c</i> (Å)	6.306 (1)	6.397(1)	6.513(3)	6.588(1)
<i>V</i> (Å ³)	1541.4(2)	1599.8(4)	1707.1(1)	1801.4(3)
<i>Z</i>	4	4	4	4
<i>D_c</i> (g/m ³)	1.586	1.528	1.541	1.460
<i>Mu</i> (mm ⁻¹)	1.689	1.627	4.151	1.451
<i>F</i> (000)	748.0	748.0	812.0	812.0
unique reflns	1981 (5699)	1057 (2983)	1322 (7112)	1567(3843)
<i>T</i> (max and min)	0.786/0.668	0.792/0.677	0.636/0.423	0.857/0.791
GOF	1.070	1.054	1.036	1.061
<i>R</i> ₁ (<i>I</i> > 2σ) ^a	0.023	0.030	0.037	0.034
<i>wR</i> ₂ (<i>I</i> > 2σ) ^b	0.060	0.075	0.091	0.072
Flack parameter	0.02(1)	0.03(2)	0.03(3)	0.00(2)
^a $R_1 = \sum F_o - F_c / \sum F_o ^2$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_c^2)^2]^{1/2}$				

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2. R. Jacobson, REQAB. Molecular Structure Corporation, The Woodlands, Texas, USA 1998.
3. T. Higashi, ABSCOR. Rigaku Corporation, Tokyo, Japan. 1995.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, **42**, 339.
5. G. M. Sheldrick, SHELXL97. University of Göttingen, Germany. 1997.
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Table S2. Selected bond distances (Å) and angles (deg) for **1** and **2**

	1α	1β	2 (103 K)	2 (353 K)
Cu1–N1	1.947(3)	1.958(2)	1.972(5)	1.956(5)
Cu1–N2	1.952(3)	1.956(2)	1.956(5)	1.943(5)
Cu1–N3	2.027(3)	2.019(2)	2.022(3)	2.031(3)
Cu1–N4	/	2.018(2)	/	/
Cu1–S1 ^B	2.879(2)	2.834(1)	2.676(2)	2.774(2)
\angle N1–Cu1–S1 ^B	94.1(2)	92.51(9)	97.1(1)	95.9(2)
\angle N1–Cu1–N3	89.10(6)	89.87(7)	88.83(7)	88.50(8)
\angle N1–Cu1–N4	/	88.30(7)	/	/
\angle N3–Cu1–S1 ^B	94.4(1)	93.79(9)	95.7(1)	94.3(1)
\angle N2–Cu1–S1 ^B	89.7(2)	90.4(1)	95.0(2)	96.3(2)
\angle N2–Cu1–N1	176.3(3)	177.0(1)	167.9(2)	167.8(2)
\angle N2–Cu1–N3	90.61(6)	90.66(8)	89.99(8)	90.58(8)
\angle N2–Cu1–N4	/	90.65(8)	/	/
\angle N4–Cu1–S1 ^B	/	96.38(9)	/	/
\angle N4–Cu1–N3	/	169.7(1)	/	/
Symmetry codes	B) 1–x, 2–y, 1/2+z.		B) 1–x, 2–y, –1/2+z.	

Table S3. Interchain hydrogen-bonds geometry (Å, deg) for **1** and **2**

	D–H \cdots A	H \cdots A	D \cdots A	D–H \cdots A
1α	N4#–H \cdots S2	2.509(3)	3.426(6)	150.9(3)
1β	N5#–H \cdots S2	2.85(4)	3.545(3)	169(4)
	N6\$–H \cdots S2	2.82 (4)	3.490(4)	146(3)
2 (103 K)	N4#–H \cdots S2	2.69(4)	3.485(3)	155(4)
2 (353 K)	N4#–H \cdots S2	2.89(6)	3.597(4)	148(5)

Symmetry codes: for **1 α** , #) –0.5+x, 1.5–y, –0.5+z; for **1 β** , #) –0.5+x, 1.5–y, –0.5+z; \$) 0.5+x, 1.5–y, –0.5+z; for **2 (103 K)**, #) 0.5–x, 1.5–y, –0.5+z; for **2 (353 K)**, #) 0.5+x, 1.5–y, 0.5+z.

Table S4. Selected structural parameters (Å, deg) of NCS[–] groups

	1 α	1 β	2 (103 K)	2 (353 K)
C1–N1	1.138(5)	1.148(3)	1.156(6)	1.161(6)
C1–S1	1.630(3)	1.641(3)	1.640(5)	1.627(5)
\angle N1–C1–S1	179.4(5)	179.1(3)	179.8(6)	179.6(5)
C2–N2	1.154(8)	1.158(4)	1.163(7)	1.149(8)
C2–S2	1.671(9)	1.630(3)	1.634(5)	1.645(6)
\angle N2–C2–S2	155(2)	178.5(3)	180.0(5)	179.8(5)

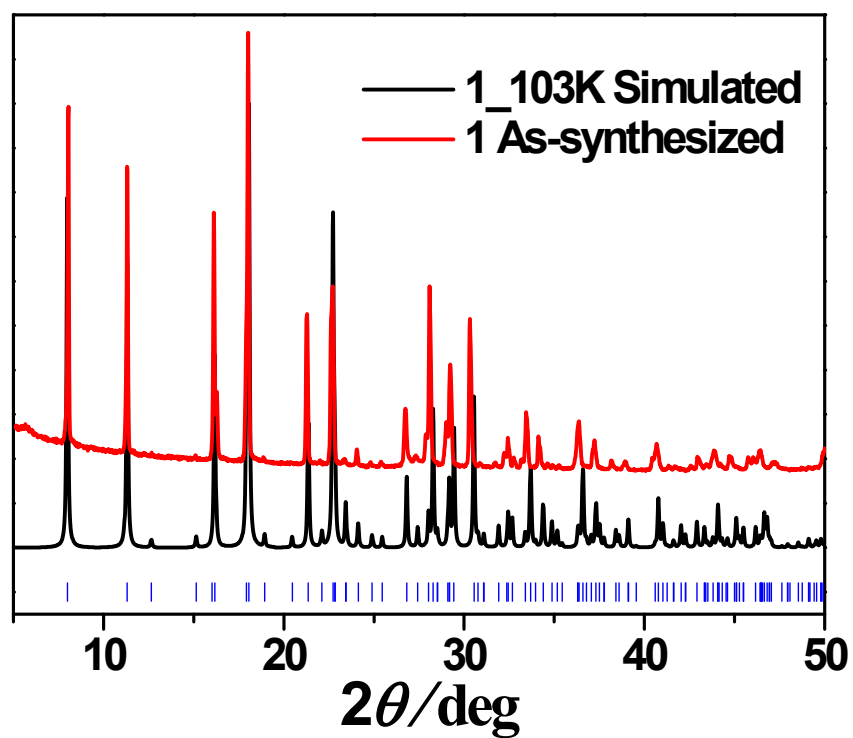


Fig. S1 Powder X-ray diffraction (PXRD) patterns of **1** at room temperature

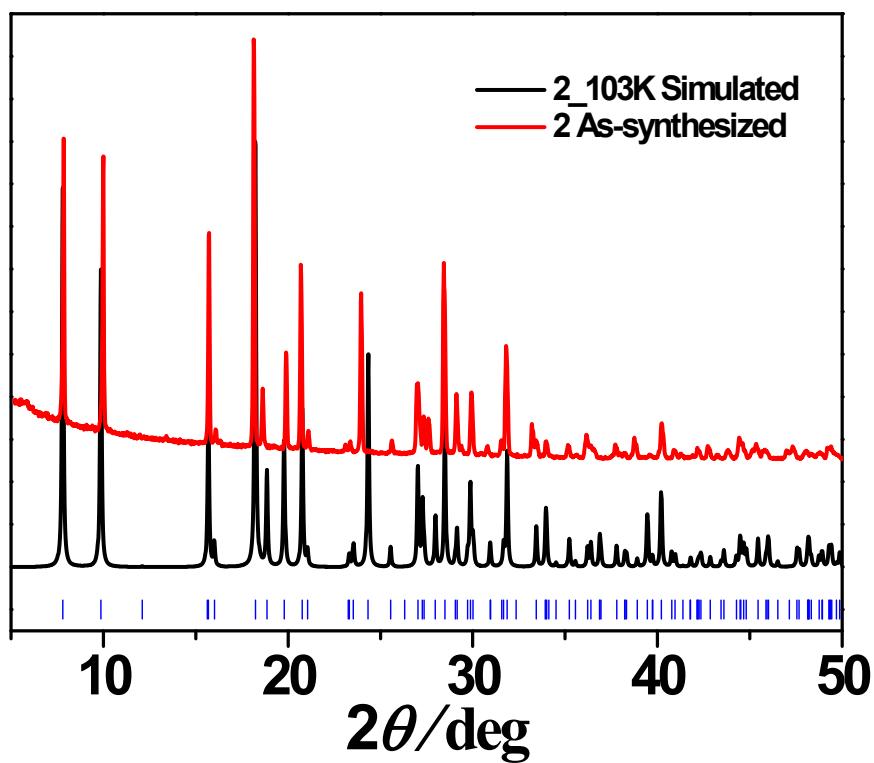


Fig. S2 Powder X-ray diffraction (PXRD) patterns of **2** at room temperature

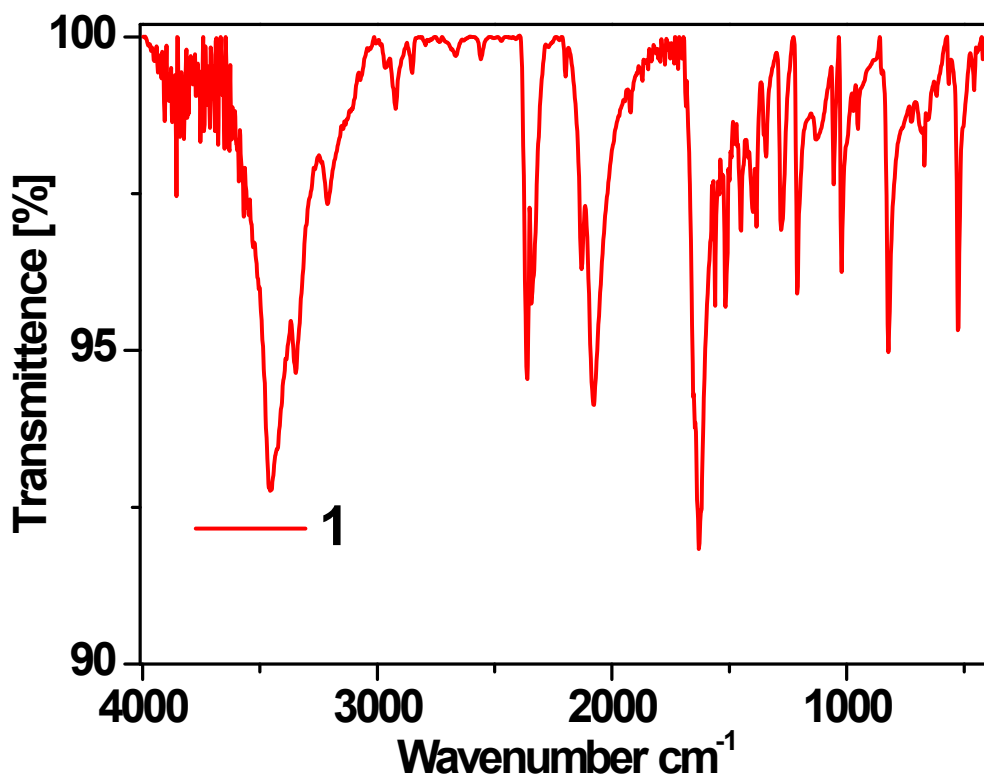


Fig. S3. The FT-IR spectra of **1** at room temperature

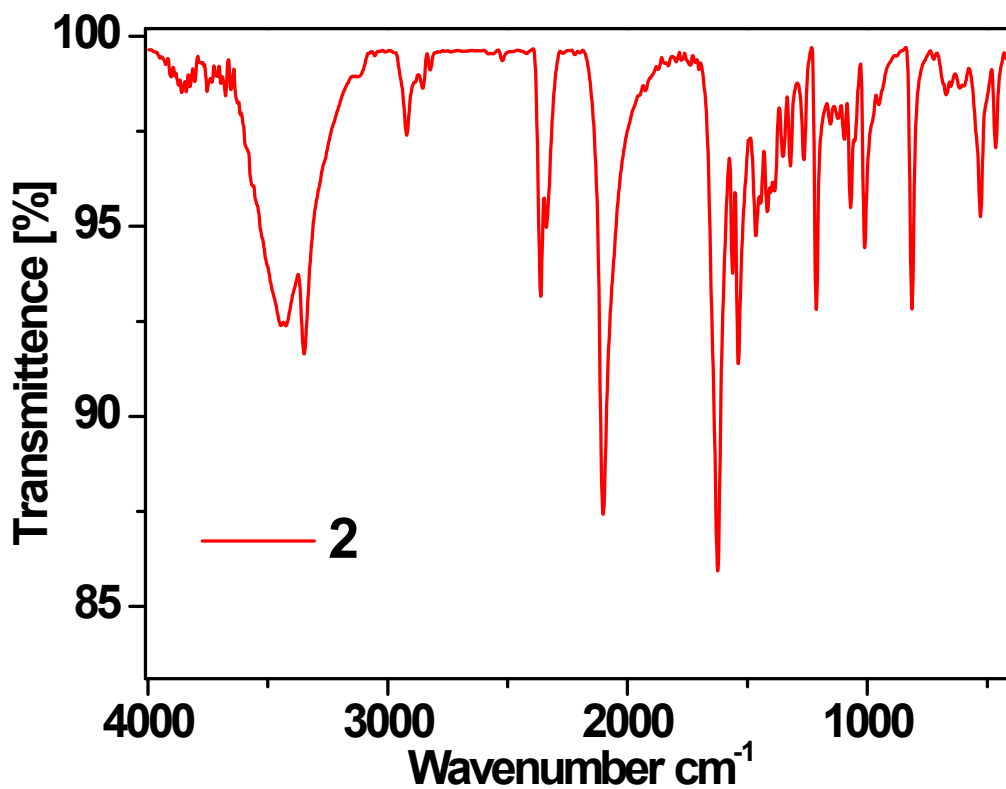


Fig. S4. The FT-IR spectra of **2** at room temperature

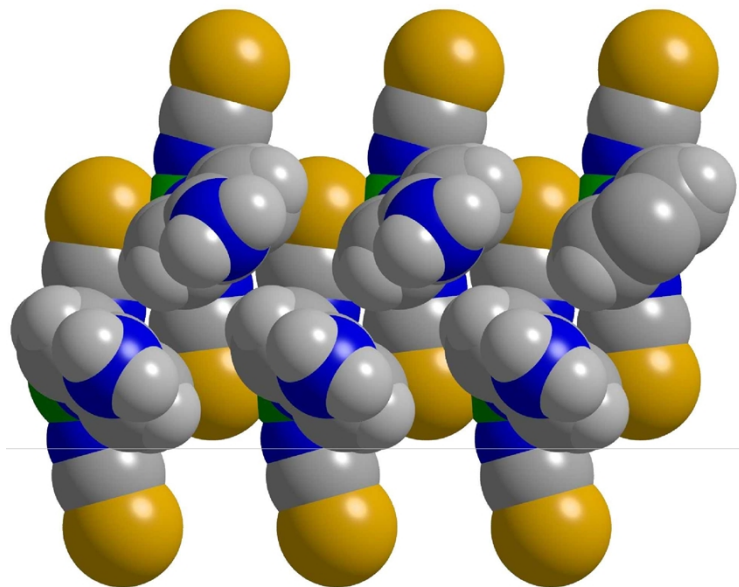


Fig. S5. The herringbone array of 4-APy ligands in the $[\text{Cu}(\text{NCS})_2(4\text{-APy})]_n$ chain of **1a**

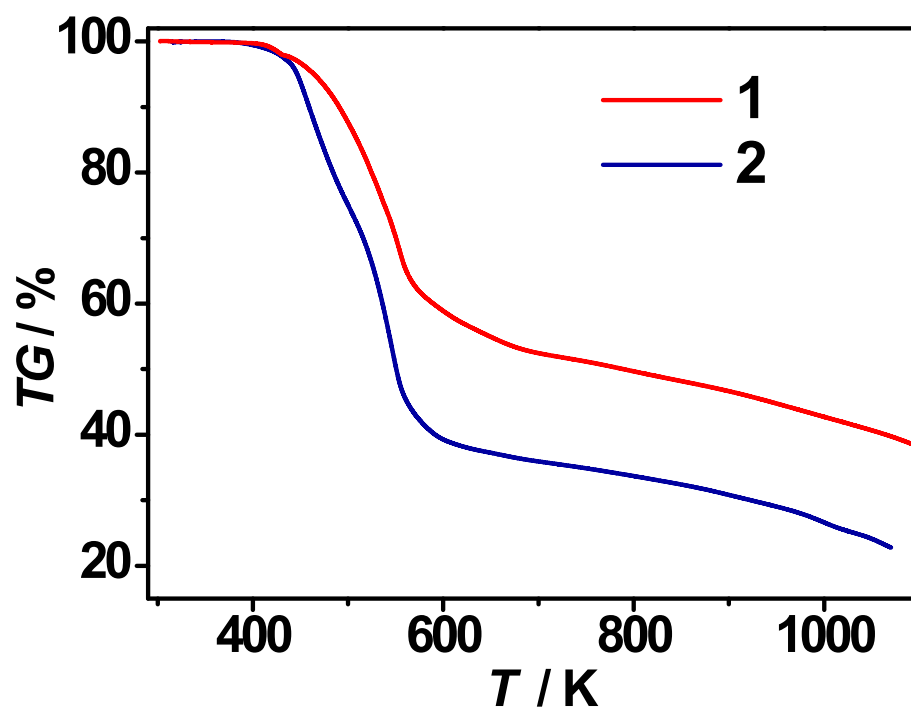


Fig. S6. TG profiles of **1** and **2**

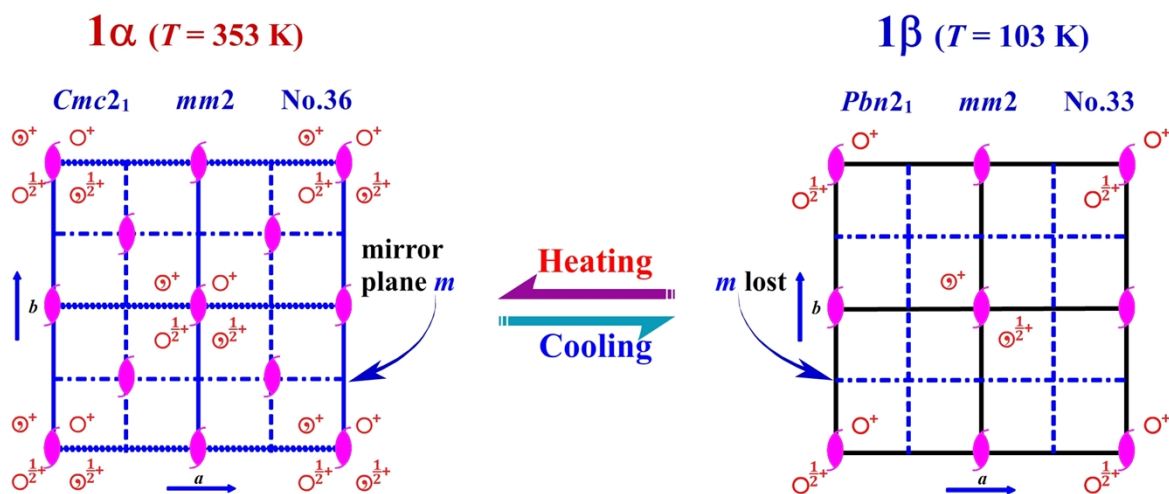


Fig. S7 The symmetry breaking process of **1** from the **1 α** to **1 β**

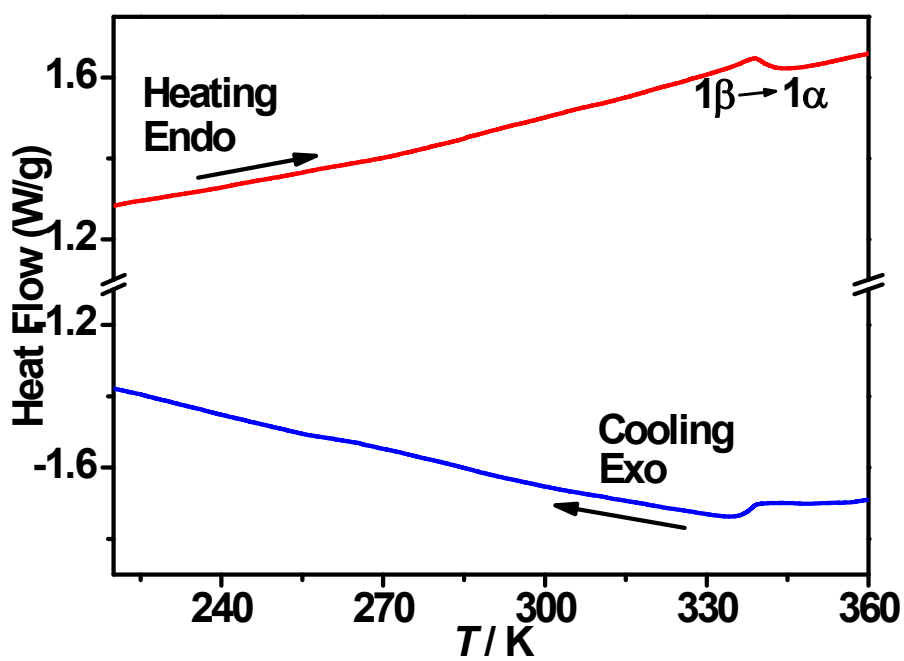


Fig. S8 DSC profile of **1** in a heating-cooling cycle

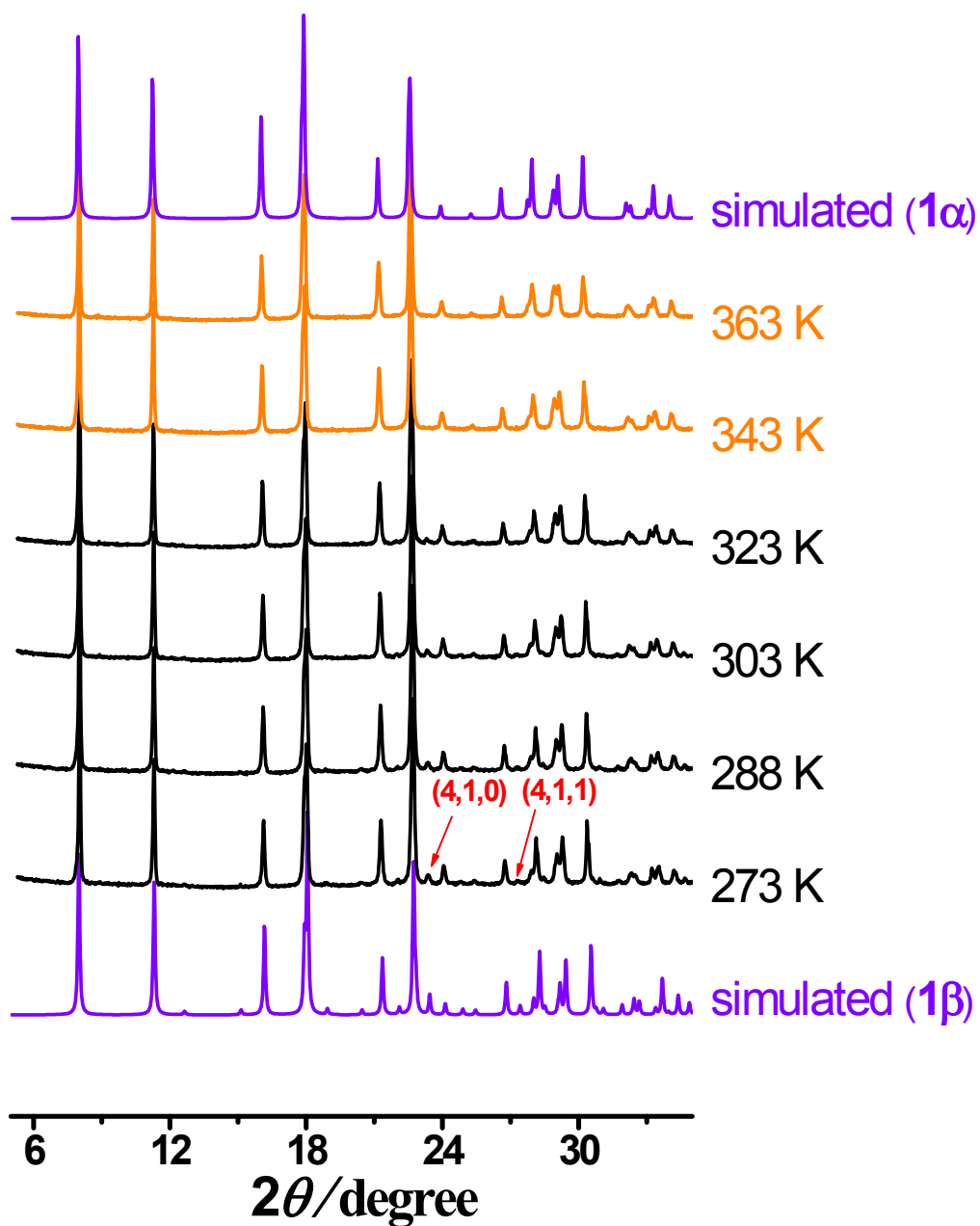


Fig. S9. The variable-temperature powder XRD patterns of **1**. Note that the intensities of diffraction peaks (4,1,0), (4,1,1) became weaker and disappeared when the sample was heated up to 343 K, which is consistent with the systematic absence required for a *C*-centered cell ($h+k \neq 2n$) in 1α , confirming the phase transition for the bulk sample.

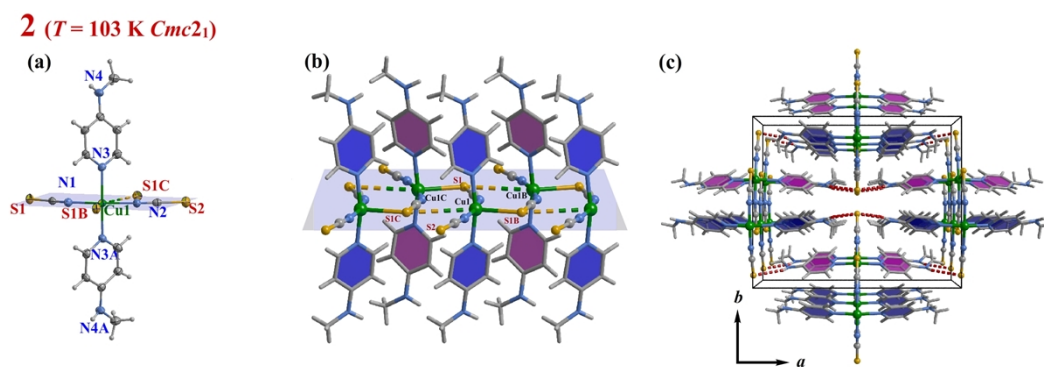


Fig. S10. The coordination environments of Cu^{2+} ion (a), $[\text{Cu}(\text{NCS})_2(4\text{-MeAPy})]_n$ chain (b) and crystal packing (c) of **2**, Symmetry codes: B) $1-x, 2-y, 0.5+z$; B) $1-x, 2-y, -0.5+z$.

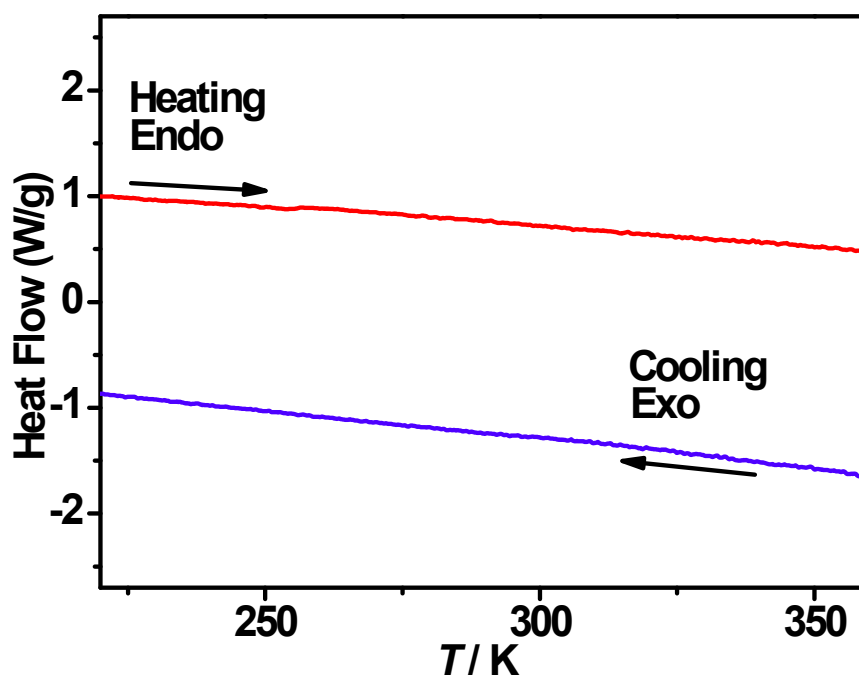


Fig. S11. DSC profile of **2** in a heating-cooling cycle