

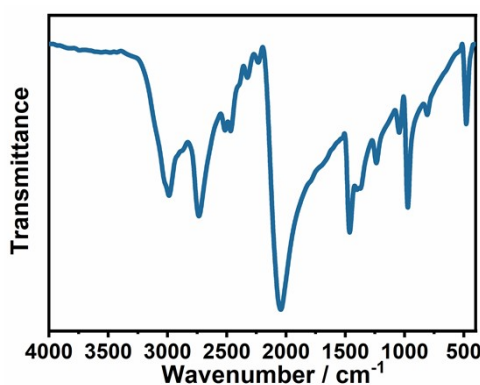
## Supporting information

### Structural phase transition and dielectric relaxation in an organic-inorganic hybrid compound: [(CH<sub>3</sub>)<sub>3</sub>NH]<sub>4</sub>[Fe(SCN)<sub>6</sub>]Cl

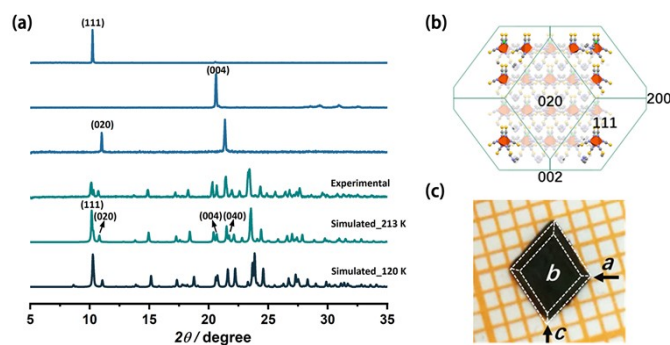
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**Fig. S1** Infrared spectrum of **1** in KBr pellet recorded at room temperature.



**Fig. S2** (a) The powder XRD patterns of **1** for the simulated at 120 and 213 K, experimental at room temperature and single crystals along different directions (020, 004 and 111). (b) The calculated BFDH morphology of **1** from Mercury. (c) The crystal picture of **1**. The *a*-, *b*- and *c*-axis were determined by XRD patterns and BFDH morphology.

**Table S1.** Summary of crystal data and structural refinements of **1** at 120 and 213 K.

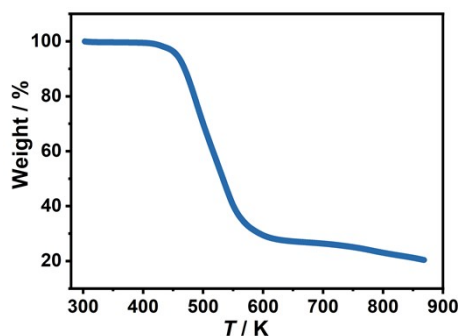
Empirical formula	[(CH <sub>3</sub> ) <sub>3</sub> NH] <sub>4</sub> [Fe(SCN) <sub>6</sub> ]Cl	
Formula weight	680.26	
Phase type	LTP	HTP
<i>T</i> / K	120(2)	213(2)
Space group	<i>Pbn</i> 2 <sub>1</sub>	<i>Aba</i> 2
<i>a</i> / Å	12.756(1)	12.806(2)
<i>b</i> / Å	15.994(2)	16.361(3)
<i>c</i> / Å	17.118(2)	17.171(3)
<i>V</i> / Å <sup>3</sup>	3492.3(5)	3597.4(11)
<i>Z</i>	4	4
<i>D</i> <sub>calcd</sub> / g cm <sup>-3</sup>	1.294	1.256
<i>μ</i> / mm <sup>-1</sup>	0.892	0.866
GOF	1.090	1.058
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0760, 0.2068	0.0805, 0.2031
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1095, 0.2344	0.1668, 0.2632
Flack parameter	-0.03(5)	-0.08(8)

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

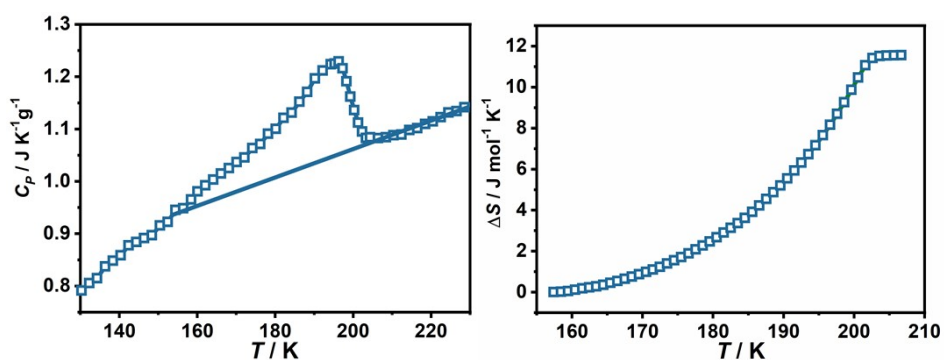
**Table S2.** The geometry (Å, °) of hydrogen bonds for **1** at 120 and 213 K.

	D–H⋯A	D–H	H⋯A	D⋯A	∠D–H⋯A
120 K	N7–H7⋯Cl1	0.980	2.210	3.157	162.17
	N8–H8⋯Cl1	0.980	2.226	3.142	155.04
	N9–H9⋯Cl1	0.980	2.146	3.113	168.98
213 K	N4–H4⋯Cl1 <sup>a</sup>	0.980	2.343	3.276	158.89
	N5–H5⋯Cl1 <sup>b</sup>	0.980	2.183	3.077	150.91
	N5'–H5'⋯Cl1 <sup>b</sup>	0.980	2.256	3.209	163.85

Symmetry codes: <sup>a</sup>) *x*-1/2, -*y*, *z*+1/2; <sup>b</sup>) *x*-1, *y*, *z*



**Fig. S3** Thermogravimetric curve measured at a rate of  $5 \text{ K min}^{-1}$  under  $\text{N}_2$  atmosphere of **1**. It reveals that compound **1** was stable up to about 413 K.



**Fig. S4** The baseline (left) and calculated  $\Delta S$  (right) related to the phase transition as a function of temperature.

**Table S3.** The relaxation time ( $\tau$ ) and distribution parameter ( $\alpha$ ) at 175, 180, 185 and 190 K along the  $a$ -,  $b$ - and  $c$ -axis for **1**.

	$T$	175 K	180 K	185 K	190 K
$a$ -axis	$\tau \times 10^6 \text{ s}$	0.80	0.53	0.27	0.14
	$\alpha$	0.003	0.003	0.004	0.004
$b$ -axis	$\tau \times 10^6 \text{ s}$	1.59	0.80	0.40	0.18
	$\alpha$	0.007	0.007	0.009	0.008
$c$ -axis	$\tau \times 10^6 \text{ s}$	8.85	2.27	0.94	0.32
	$\alpha$	0.007	0.007	0.006	0.005