# Supporting Information

## Orientational ordering of guests induced structural phase transition coupled with switchable dielectric property in a host-guest crystal: bis(Thiourea) thiazolium chloride

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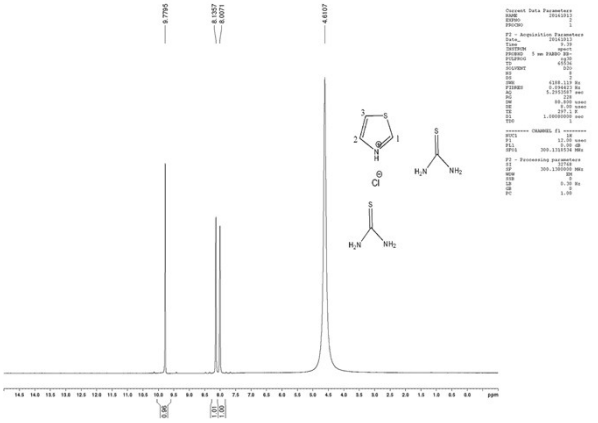

**Fig. S1** $^{1}H$ NMR ($D_2O$) spectrum of **1**.

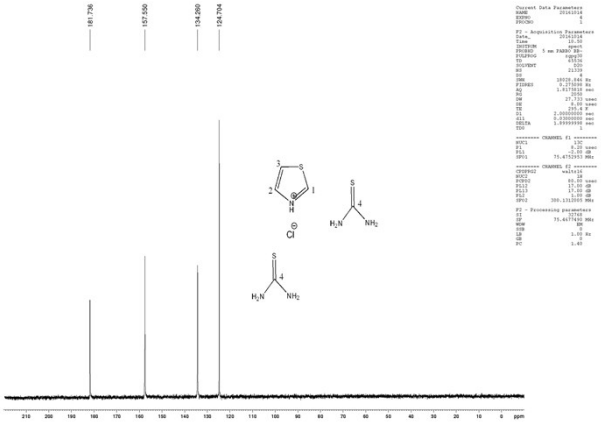

**Fig. S2** $^{13}C$ NMR ($D_2O$) spectrum of **1**.

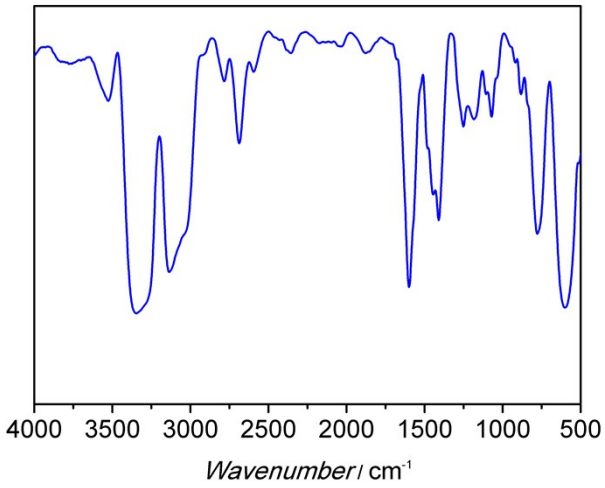


**Fig. S3** Infrared (IR) spectra of **1** measured at room temperature.

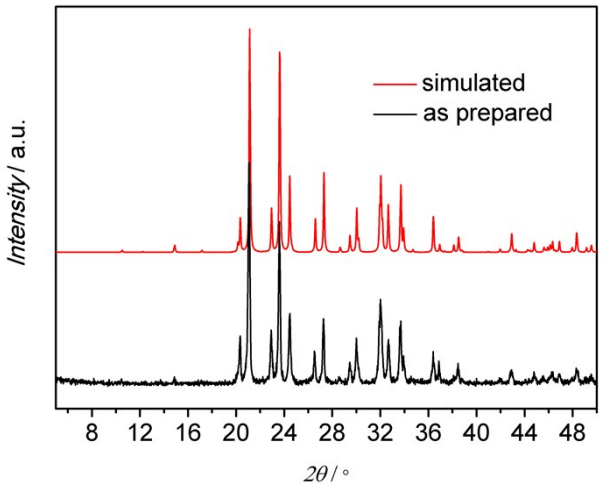


**Fig. S4** PXRD pattern for the as-prepared samples of **1** and the simulated one based on the single crystal structure at 273 K.

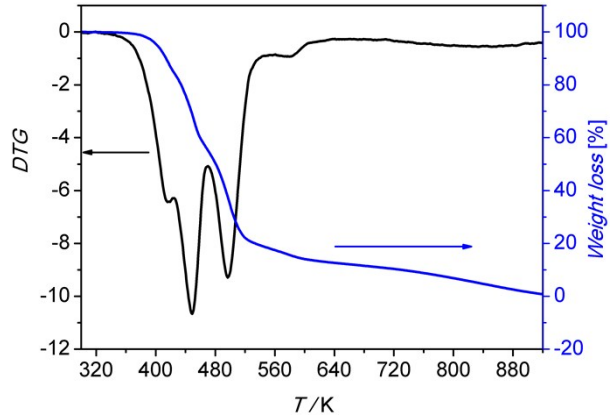


**Fig.S5** TGA measurement of **1** in the temperature range of 300−920 K.

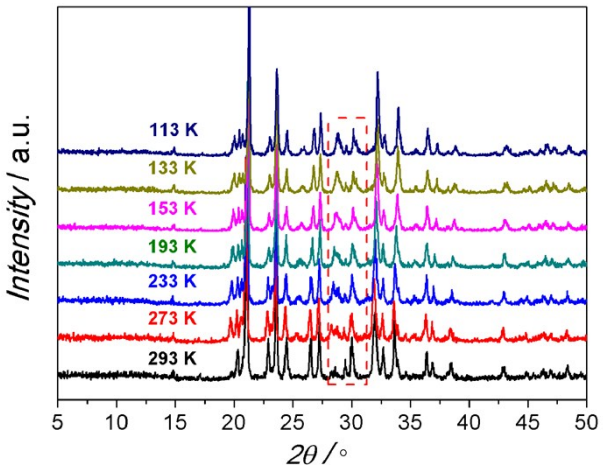


**Fig. S6** Variable-temperature PXRD pattern for the as-prepared samples of **1**.

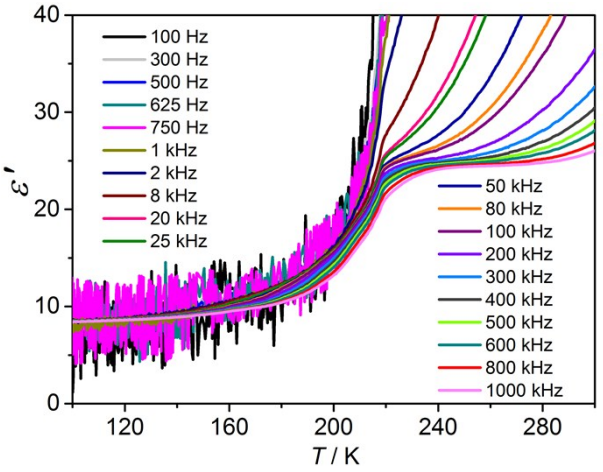


**Fig. S7** Real part of dielectric permittivity of **1** as a function of temperature at different frequencies on cooling.

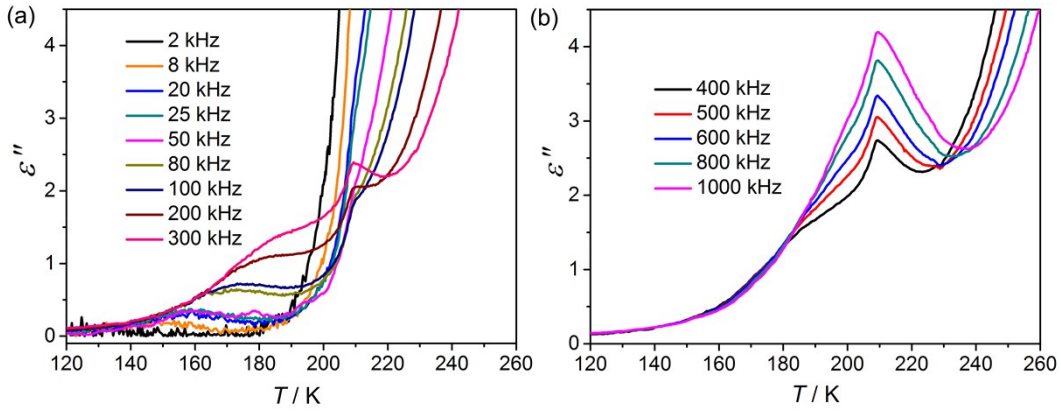


**Fig. S8** Imaginary part of dielectric permittivity of **1** as a function of temperature at different frequencies on cooling.

**Table S1**. The elemental analysis results of **1**.

| | N | C | S | H |
|---|---|---|---|---|
| 0-theoretical | 25.58 | 21.93 | 35.13 | 4.42 |
| 1-experimental | 25.23 | 21.65 | 35.52 | 4.76 |
| 2-experimental | 25.26 | 21.72 | 35.57 | 4.89 |
| 3-experimental | 25.31 | 21.55 | 35.38 | 4.84 |
| average experimental | 25.27 | 21.64 | 35.49 | 4.83 |

**Table S2**. Hydrogen bonds of **1** at 273 K and 133 K.

| | *D*–H···*A* | *D*–H | H···*A* | *D*···*A* | ∠*D*–H···*A* |
|---|---|---|---|---|---|
| 273K | N(1)–H(1A)···Cl(1)#1 | 0.86 | 2.52 | 3.307(3) | 153 |
| | N(1)–H(1B)···S(1)#2 | 0.86 | 2.54 | 3.396(4) | 175 |
| 133K | N(1)–H(1A)···Cl(1)#3 | 0.86 | 2.47 | 3.259(2) | 153 |
| | N(1)–H(1B)···S(1)#4 | 0.86 | 2.52 | 3.372(3) | 170 |
| | N(2)–H(2A)···Cl(1)#3 | 0.86 | 2.51 | 3.292(2) | 151 |
| | N(2)–H(2B)···S(1)#5 | 0.86 | 2.51 | 3.369(3) | 174 |
| | N(3)–H(3B)···S(1) | 0.86 | 2.43 | 3.320(8) | 169 |

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