

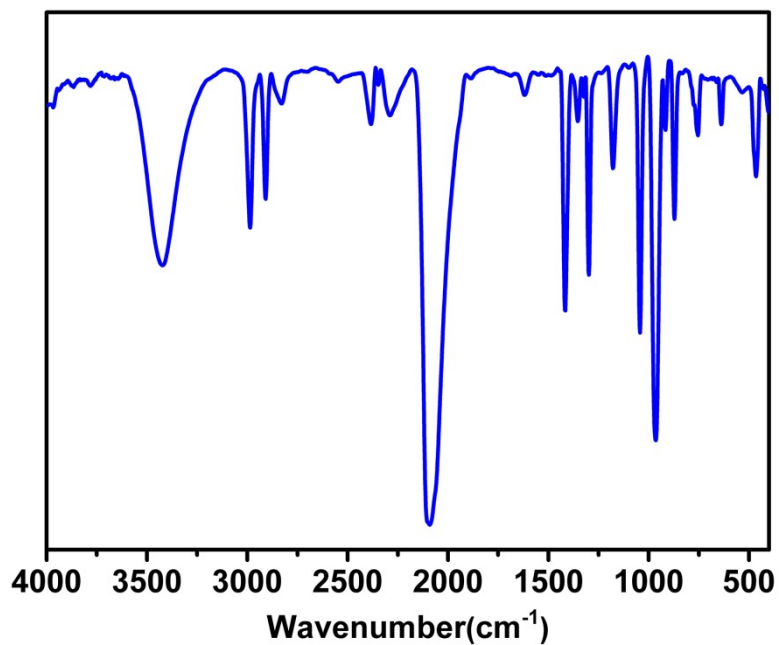
## Supporting information

### Dielectric and Nonlinear Optical Dual Switch in An Organic-inorganic Hybrid Relaxor [(CH<sub>3</sub>)<sub>3</sub>PCH<sub>2</sub>OH][Cd(SCN)<sub>3</sub>]

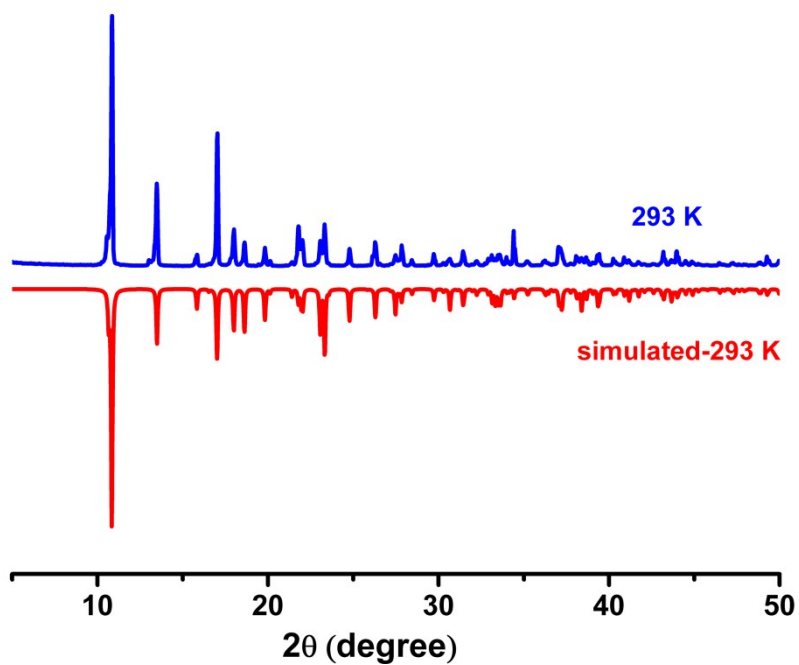
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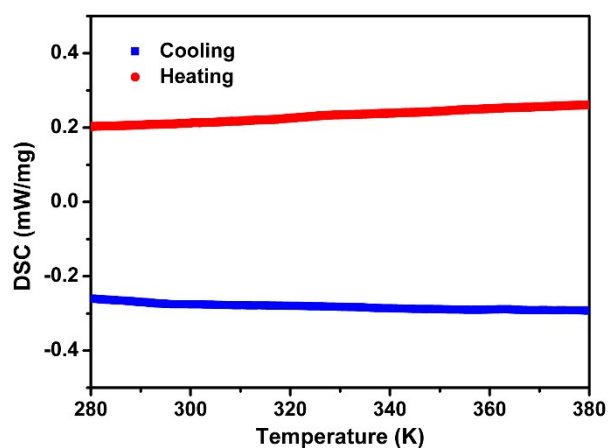
**Fig. S1** Single-crystal samples of **1**.



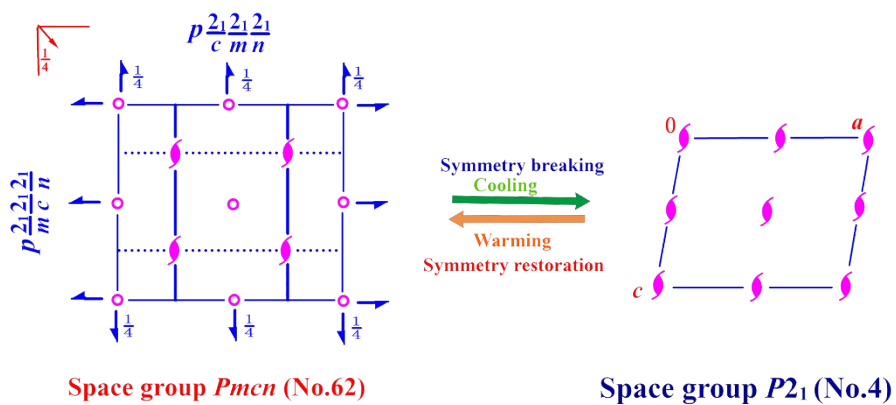
**Fig. S2.** IR spectrum of **1** measured on a KBr-diluted pellet at room temperature.



**Fig. S3** Powder XRD patterns of **1** at 293 K.



**Fig. S4** DSC curves of **1** obtained above room temperature in the cooling and heating cycles.



**Fig. S5** Transformations of space group of **1** from the RTP ( $Pmcn$ , No. 62) to LTP ( $P2_1$ , No. 4).

**Table S1** Crystal data, data collection and reduction parameter of crystals of **1** at 213 K and 293 K.

|                                                         | 213K                                                                                                        | 293K                                                               |
|---------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| Chemical Formula                                        | C <sub>14</sub> H <sub>24</sub> Cd <sub>2</sub> N <sub>6</sub> S <sub>6</sub> O <sub>2</sub> P <sub>2</sub> | C <sub>7</sub> H <sub>12</sub> CdN <sub>3</sub> S <sub>3</sub> OP  |
| Formula weight                                          | 787.5                                                                                                       | 393.75                                                             |
| Crystal system                                          | Monoclinic                                                                                                  | Orthorhombic                                                       |
| Space group                                             | <i>P</i> 2 <sub>1</sub>                                                                                     | <i>Pm</i> <i>cn</i>                                                |
| <i>a</i> , Å                                            | 10.395(6)                                                                                                   | 10.411(2)                                                          |
| <i>b</i> , Å                                            | 13.176(7)                                                                                                   | 13.112(3)                                                          |
| <i>c</i> , Å                                            | 10.742(4)                                                                                                   | 10.711(2)                                                          |
| $\beta$ , deg                                           | 92.12(4)                                                                                                    | 90                                                                 |
| <i>V</i> , Å <sup>3</sup>                               | 1470.2(13)                                                                                                  | 1462.2(5)                                                          |
| <i>Z</i>                                                | 2                                                                                                           | 4                                                                  |
| Index ranges                                            | -12 ≤ <i>h</i> ≤ 12                                                                                         | -13 ≤ <i>h</i> ≤ 13                                                |
|                                                         | -15 ≤ <i>k</i> ≤ 15                                                                                         | -12 ≤ <i>k</i> ≤ 17                                                |
|                                                         | -12 ≤ <i>l</i> ≤ 12                                                                                         | -13 ≤ <i>l</i> ≤ 13                                                |
| <i>D</i> <sub>calcd</sub> , g•cm <sup>-3</sup>          | 1.709                                                                                                       | 1.746                                                              |
| $\mu$ , mm <sup>-1</sup>                                | 1.98                                                                                                        | 2.01                                                               |
| <i>refns measured</i>                                   | 8587                                                                                                        | 9672                                                               |
| <i>independent reflns</i>                               | 5178                                                                                                        | 1760                                                               |
| <i>reflns used</i>                                      | 2656                                                                                                        | 1596                                                               |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                | 1.077                                                                                                       | 1.17                                                               |
| Final <i>R</i> indices [ <i>I</i> > 2sigma( <i>I</i> )] | <i>R</i> <sub><i>I</i></sub> =0.098, <i>wR</i> <sub>2</sub> = 0.2945                                        | <i>R</i> <sub><i>I</i></sub> =0.044, <i>wR</i> <sub>2</sub> =0.119 |

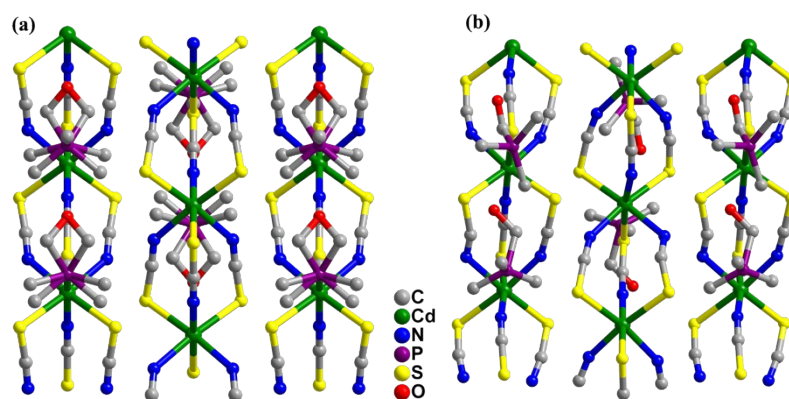
**Table S2** The key bond distances and angles of **1** at 213 K and 293 K.

|       |          |             |          |             |
|-------|----------|-------------|----------|-------------|
| 213 K | Cd1—S1   | 2.765 (5)   | S1—C1    | 1.535 (17)  |
|       | Cd1—S2   | 2.687(5)    | C1—N1    | 1.09 (2)    |
|       | Cd1—S3   | 2.734 (4)   | S2—C2    | 1.683 (17)  |
|       | Cd2—S4   | 2.738 (5)   | C2—N2    | 1.18 (2)    |
|       | Cd2—S5   | 2.713 (6)   | S3—C3    | 1.603 (16)  |
|       | Cd2—S6   | 2.739 (6)   | C3—N3    | 1.20 (2)    |
|       | Cd1—N4   | 2.323 (14)  | S4—C4    | 1.748 (14)  |
|       | Cd1—N5   | 2.339 (14)  | C4—N4    | 1.14 (2)    |
|       | Cd1—N6   | 2.412 (13)  | S5—C5    | 1.636 (17)  |
|       | Cd2—N1   | 2.343 (13)  | C5—N5    | 1.21 (2)    |
|       | Cd2—N2   | 2.466 (13)  | S6—C6    | 1.764 (16)  |
|       | Cd2—N3   | 2.303 (12)  | C6—N6    | 1.14 (2)    |
|       | S1—C1—N1 | 170.2 (18)  | S4—C4—N4 | 173.1 (16)  |
|       | S2—C2—N2 | 169.3 (17)  | S5—C5—N5 | 176.1 (18)  |
|       | S3—C3—N3 | 172.2 (17)  | S6—C6—N6 | 160.06 (17) |
| 293 K | Cd1—S1i  | 2.7154 (15) | C1—S1    | 1.626 (5)   |
|       | Cd1—S2   | 2.7183 (18) | C1—N1    | 1.162 (6)   |
|       | Cd1—N1   | 2.377 (5)   | C2—S2    | 1.636 (6)   |
|       | Cd1—N2i  | 2.284 (6)   | C2—N2    | 1.147 (8)   |
|       | S1—C1—N1 | 174.8(5)    | S2—C2—N2 | 179.3 (5)   |

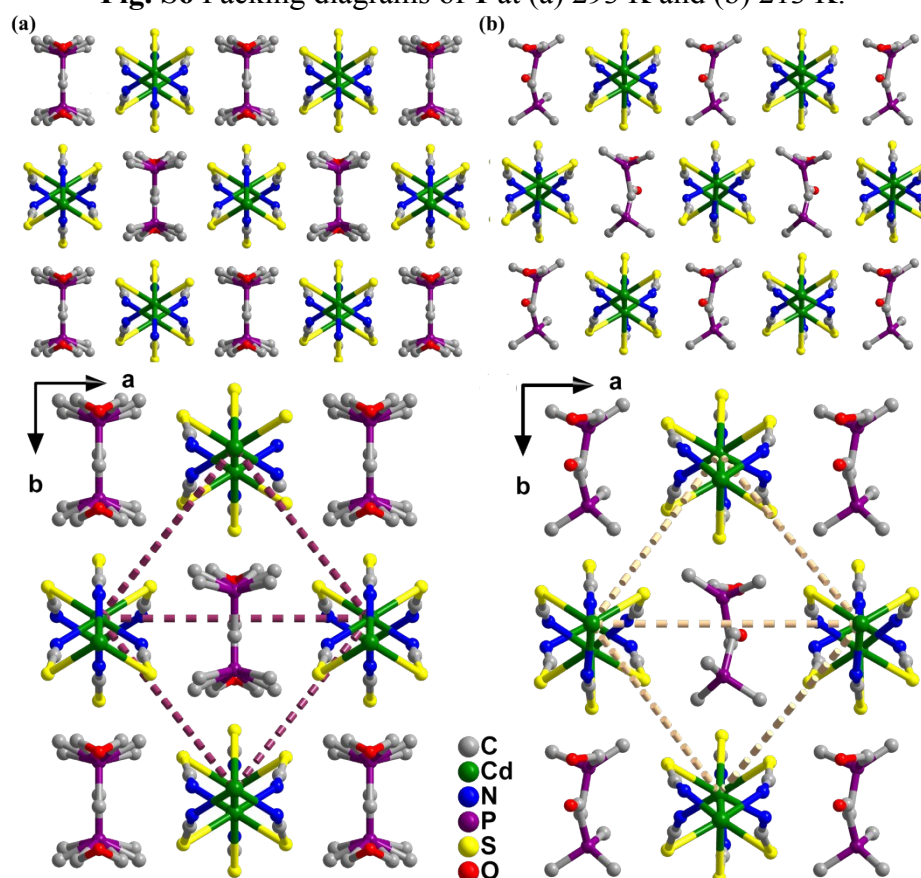
symmetry codes: (i) (x, -y+1/2, z-1/2)

**Table S3** The torsion angels of the ligand in **1** at 213 K and 293 K

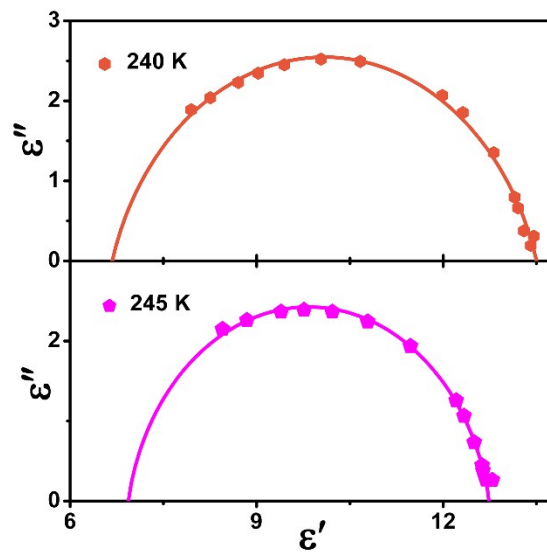
|       |              |            |
|-------|--------------|------------|
| 213 K | Cd1—S1—C1—N1 | 118.98(10) |
|       | Cd1—S2—C2—N2 | 117.73(14) |
|       | Cd1—S3—C3—N3 | 155.53(11) |
|       | Cd2—S4—C4—N4 | 167.52(13) |
|       | Cd2—S5—C5—N5 | 160.17(24) |
|       | Cd2—S6—C6—N6 | 119.73(47) |
| 293 K | Cd1—S1—C1—N1 | 174.80(51) |
|       | Cd1—S2—C2—N2 | 180.00(35) |



**Fig. S6** Packing diagrams of **1** at (a) 293 K and (b) 213 K.



**Fig. S7** The packing view of **1** along the  $c$  axis at (a) 293 K and (b) 213 K.



**Fig. S8** Cole-Cole diagrams for the polycrystalline sample of **1** at 240 K and 245 K.

**Table S4** Temperature-dependence of the dielectric parameters of **1**: dielectric increment ( $\epsilon_0 - \epsilon_\infty$ ), relaxation time ( $\tau$ ), and distribution parameter ( $\alpha$ ).

| $T$ (K) | $\epsilon_\infty$ | $\epsilon_0$ | $\tau \times 10^6$ s | $\alpha$ |
|---------|-------------------|--------------|----------------------|----------|
| 225     | 6.14              | 10.24        | 18.56                | 0.33     |
| 230     | 6.27              | 10.99        | 9.47                 | 0.25     |
| 235     | 6.34              | 12.44        | 4.97                 | 0.16     |
| 240     | 6.54              | 13.56        | 2.68                 | 0.11     |
| 245     | 6.95              | 12.71        | 1.48                 | 0.14     |