Multiple structural transformations coupled with switchable magnetic and dielectric responses in an amphidynamic crystal of 4'-tert-butylbenzylpyridinium bis(maleonitriledithiolate)nickelate

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Figure S1 the packing structure of 1 at 89 K in LT phase.

Table S1: Characteristic bond lengths (Å) and angles (°) in $[Ni(mnt)_2]^-$ moiety at 200 K in **HT** and 170K in **IT** phase



| Tomp | 200 K 170 K | | | | | | | |
|-----------|-------------|-------|-------|-------|-------|-------|-------|--|
| remp. | 200 K 1/0 K | | | | | | | |
| Dist. / Å | Ni1 | Ni1 | Ni2 | Ni3 | Ni4 | Ni5 | Ni6 | |
| ∠1 / ° | 92.55 | 92.45 | 92.54 | 92.55 | 92.58 | 92.48 | 92.64 | |
| ∠2 / ° | 88.51 | 85.93 | 89.01 | 87.02 | 87.90 | 88.68 | 85.52 | |
| ∠3 / ° | 92.42 | 92.69 | 92.40 | 92.54 | 92.38 | 92.71 | 92.21 | |
| ∠4 / ° | 86.50 | 88.91 | 86.00 | 87.88 | 87.10 | 86.21 | 89.62 | |
| a1 / Å | 2.142 | 2.134 | 2.151 | 2.143 | 2.140 | 2.140 | 2.138 | |
| a2 / Å | 2.144 | 2.146 | 2.146 | 2.146 | 2.145 | 2.156 | 2.139 | |
| a3 / Å | 2.136 | 2.146 | 2.134 | 2.146 | 2.138 | 2.138 | 2.144 | |
| a4 / Å | 2.144 | 2.149 | 2.143 | 2.142 | 2.149 | 2.144 | 2.153 | |
| b1 / Å | 1.725 | 1.720 | 1.733 | 1.724 | 1.733 | 1.719 | 1.728 | |
| b2 / Å | 1.712 | 1.720 | 1.722 | 1.723 | 1.716 | 1.724 | 1.717 | |
| b3 / Å | 1.717 | 1.732 | 1.715 | 1.723 | 1.713 | 1.721 | 1.718 | |
| b4 / Å | 1.715 | 1.716 | 1.720 | 1.719 | 1.727 | 1.705 | 1.729 | |

| $\begin{array}{c} b1 \\ c 1 \\ c 1 \\ b 4 \\ c 4 \\ a 3 \\ b 3 \\ c 1 \\ b 4 \\ c 1 \\ b 3 \\ c 1 \\ c 2 \\ c 2 \\ c 1 \\ c 2 \\ $ | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|--|--|
| Temp. | 89 K | | | | | | | |
| | Ni1 | Ni2 | Ni3 | Ni4 | Ni5 | Ni6 | | |
| ∠1 / ° | 92.43 | 92.59 | 92.59 | 92.59 | 92.59 | 92.66 | | |
| ∠2 / ° | 85.88 | 89.14 | 87.37 | 87.37 | 88.59 | 85.13 | | |
| ∠3 / ° | 92.72 | 92.37 | 92.55 | 92.43 | 92.94 | 92.28 | | |
| ∠4 / ° | 88.96 | 85.83 | 87.48 | 87.59 | 85.98 | 89.95 | | |
| a1 / Å | 2.137 | 2.151 | 2.143 | 2.136 | 2.139 | 2.141 | | |
| a2 / Å | 2.150 | 2.150 | 2.154 | 2.150 | 2.161 | 2.140 | | |
| a3 / Å | 2.147 | 2.140 | 2.146 | 2.133 | 2.136 | 2.143 | | |
| a4 / Å | 2.150 | 2.144 | 2.145 | 2.155 | 2.146 | 2.157 | | |
| b1 / Å | 1.723 | 1.731 | 1.730 | 1.736 | 1.720 | 1.724 | | |
| b2 / Å | 1.715 | 1.723 | 1.729 | 1.729 | 1.723 | 1.726 | | |
| b3 / Å | 1.737 | 1.719 | 1.737 | 1.717 | 1.734 | 1.722 | | |
| b4 / Å | 1.721 | 1.722 | 1.729 | 1.717 | 1.711 | 1.728 | | |

Table S2: Characteristic bond lengths (Å) and angles (°) in $[Ni(mnt)_2]^-$ moiety at 89 K in LT phase

Table S3: Typical intermolecular distances in onion dimers and cation dimers at 200 K, 170 K and 89 K

| d4 d5 d1 d3 d2 | | | | | | | | | |
|-------------------|----------|-----------|----------|----------|----------|----------|----------|--|--|
| Temp./K | 200 | | 170 | | | 89 | | | |
| Dist./ Å | Ni1-Ni1 | Ni1-Ni2 | Ni3-Ni4 | Ni5-Ni6 | Ni1-Ni2 | Ni3-Ni4 | Ni5-Ni6 | | |
| d 1 | 4.100(1) | 4.186(1) | 4.132(1) | 4.387(1) | 4.182(1) | 4.150(1) | 4.100(1) | | |
| d2 | 4.053(1) | 4.178(1) | 4.072(1) | 4.668(1) | 4.169(0) | 4.156(3) | 4.497(2) | | |
| d3 | 4.057(1) | 4.035 (1) | 4.150(1) | 4.267(1) | 4.029(2) | 4.093(2) | 4.259(2) | | |
| d4 | 3.804(1) | 3.834(1) | 3.744(1) | 3.627(1) | 4.304(2) | 4.269(2) | 4.586(2) | | |
| d5 | 4.185(1) | 4.312(1) | 4.241(1) | 4.593(1) | 3.821(2) | 3.683(2) | 3.604(2) | | |



-0.2

-0.4

-0.6 + -200

Exo Up

Figure S2 DSC plot of 1.

-150



-83.95°C

Temperature (°C)

-50

ċ

50

Universal V4.5A TA Instrum

-100

Figure S3 PXRD plots of **1** (red lines: experimental profiles and black lines: simulated profiles).



Figure S4 Plots of dielectric permittivity ε' against temperature *T* at selected ac frequencies for a single crystal of **1** and the measurement was carried out upon heating (143–353 K).



Figure S5 IR plots of 1.