Giant barocaloric tunability in

\[ [(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Cd}[\text{N(CN)}_2]_3 \] hybrid perovskite

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Figure S1. Thermogravimetric data taken for [TPrA]Cd[dca]$_3$ on heating from room temperature to 1173 K.
Figure S2. Off-centre displacements of the TPrA cations in the polymorph P0. All the TPrA cations, which are represented here using green and red arrows, display off-centre shifts towards the CdN₆ octahedra located in the corners of the pseudocuboctahedral cavities. TPrA cations are coloured here according to the direction of their off-centre shift; octahedra at the corners of the pseudocuboctahedral cavities are coloured according to the shift of the TPrA cation inside their corresponding cavity. These displacements lead to an antiparallel arrangement of the TPrA cations along the b axis. Note: all atoms other than Cd atoms, and all atomic bonds, have been omitted to facilitate the visualization of the displacements.
Figure S3. Off-centre displacements of the TPRA cations in the polymorph PI. Half of the TPRA cations, which are represented here using green circles and red crosses, display off-centre shifts along the c axis that follow an antiferrodistorsive up-down/up-down pattern (green circles indicate out-of-plane shifts towards the upper face of the pseudocuboctahedral cavity; red crosses indicate into-the-plane shifts towards the bottom face of the cavity. Blue circles represent the other half of TPRA cations, which remain centred in the pseudocuboctahedral cavities. CdN₆ octahedra are represented in beige. All atoms and bonds have been omitted to facilitate the visualization of the structure.
Figure S4. Columnar shifts in the polymorph PI, represented using plan views along (a) the $a$ axis, and (b) the $c$ axis. Columnar shifts are active and out-of-phase along all three crystallographic axis, as indicated by the yellow arrows. Projected unit cells are shown using blue lines.
Figure S5. Le Bail refinement of x-ray powder diffraction data taken at 380 K, for the polymorph P1b. Red symbols are experimental data, black lines are fitted patterns, green lines indicate indexed reflections.
Figure S6. Temperature-dependent unit-cell volume near the ~385 K orthorhombic-tetragonal phase transition (black dashed line), obtained via Le Bail refinement of powder x-ray diffraction data. The thermal expansion, and therefore the corresponding additional changes in pressure-driven isothermal entropy, are similar either side of the transition.
Table S1. Crystallographic data for the polymorphs P0, PI and PII, obtained from single-crystal x-ray diffraction performed at 100, 300 and 390 K (data at 200 K are not shown because our [TPrA]Cd[dca]3 perovskite displays the same polymorph at 100 K and 200 K). The table also shows partial crystallographic data for the polymorph PIIb structure, which were obtained at 380 K via Le Bail refinement of powder x-ray diffraction data.

<table>
<thead>
<tr>
<th></th>
<th>P0</th>
<th>PI</th>
<th>PIIb</th>
<th>PII</th>
</tr>
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<td>Formula</td>
<td>C18H28N10Cd</td>
<td>C18H28N10Cd</td>
<td>C18H28N10Cd</td>
<td>C18H28N10Cd</td>
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<tr>
<td>Formula weight/g mol⁻¹</td>
<td>496.90</td>
<td>496.90</td>
<td>496.90</td>
<td>496.90</td>
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<td>Temperature/K</td>
<td>100(2)</td>
<td>300(2)</td>
<td>380(2)</td>
<td>390(2)</td>
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<tr>
<td>Crystal system</td>
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<td>Tetragonal</td>
<td>Orthorhombic</td>
<td>Tetragonal</td>
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<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P4₂₁c</td>
<td>Ibam</td>
<td>I4/mcm</td>
</tr>
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<td>a/Å</td>
<td>16.2377(6)</td>
<td>16.3047(4)</td>
<td>11.6398(9)</td>
<td>11.6728(13)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.5366(6)</td>
<td>11.6739(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c/Å</td>
<td>17.4934(7)</td>
<td>17.6047(5)</td>
<td>17.764(1)</td>
<td>17.818(2)</td>
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<tr>
<td>β/°</td>
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<td>90.000</td>
<td>90.000</td>
<td>90.000</td>
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<td>Unit cell volume/Å³</td>
<td>4412.9(3)</td>
<td>4680.1(3)</td>
<td>2413.9(18)</td>
<td>2427.8(6)</td>
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<td>No. of formula units per unit cell, Z</td>
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<td>8</td>
<td>4</td>
<td>4</td>
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<td>No. of reflections measured</td>
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<td>114578</td>
<td>-</td>
<td>2539</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>9062</td>
<td>4854</td>
<td>-</td>
<td>680</td>
</tr>
<tr>
<td>(R_{\text{int}}) values (I &gt; 2σ(I))</td>
<td>0.0000</td>
<td>0.0515</td>
<td>-</td>
<td>0.0240</td>
</tr>
<tr>
<td>Final (R_{1}) values (I &gt; 2σ(I))</td>
<td>0.0354</td>
<td>0.0358</td>
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<td>0.0468</td>
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<td>Final (wR_{2}(F^2)) values (I &gt; 2σ(I))</td>
<td>0.0812</td>
<td>0.0941</td>
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<td>Final (R_{1}) values (all data)</td>
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<td>Goodness of fit on (F^2)</td>
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<td>1.060</td>
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Table S2. Selected bond lengths and bond angles for the polymorph P0 of our [TPrA]Cd[dca].

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<thead>
<tr>
<th>bond length (Å)</th>
<th>Cd 100 K</th>
<th>bond angle (°)</th>
<th>Cd 100 K</th>
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<tbody>
<tr>
<td>Cd2-N1</td>
<td>2.324(3)</td>
<td>Cd2-N1-C1</td>
<td>178.5(3)</td>
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<tr>
<td>Cd2-N2</td>
<td>2.354(3)</td>
<td>Cd2-N2-C2</td>
<td>166.0(3)</td>
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<tr>
<td>Cd2-N3</td>
<td>2.309(3)</td>
<td>Cd2-N3-C3</td>
<td>177.1(3)</td>
</tr>
<tr>
<td>Cd2-N4</td>
<td>2.335(3)</td>
<td>Cd2-N4-C4</td>
<td>128.4(3)</td>
</tr>
<tr>
<td>Cd2-N5</td>
<td>2.313(3)</td>
<td>Cd2-N5-C5</td>
<td>139.6(3)</td>
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<tr>
<td>Cd2-N6</td>
<td>2.305(3)</td>
<td>Cd2-N6-C6</td>
<td>167.3(3)</td>
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<td>Cd1-N8</td>
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<td>Cd1-N8-C7</td>
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<td>Cd1-N9</td>
<td>2.326(3)</td>
<td>Cd1-N9-C8</td>
<td>144.8(3)</td>
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<tr>
<td>Cd1-N10</td>
<td>2.315(3)</td>
<td>Cd1-N10-C9</td>
<td>172.7(3)</td>
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<tr>
<td>Cd1-N11</td>
<td>2.317(3)</td>
<td>Cd1-N11-C10</td>
<td>168.0(3)</td>
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<tr>
<td>Cd1-N12</td>
<td>2.310(3)</td>
<td>Cd1-N12-C11</td>
<td>148.8(3)</td>
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<td>Cd1-N13</td>
<td>2.337(3)</td>
<td>Cd1-N13-C11</td>
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<td>Cd-Cd (c axis)</td>
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<td></td>
<td>8.8361(5)</td>
<td>Cd1-N10-C10</td>
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<td>8.1077(4)</td>
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<td>8.3173(4)</td>
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Table S3. Selected bond lengths and bond angles for the polymorph PI of our [TPrA]Cd[dca]$_3$.

<table>
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<th>bond length (Å)</th>
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<tr>
<td>Cd-N1</td>
<td>2.308(5)</td>
<td>Cd-N1-C4</td>
<td>174.2(7)</td>
</tr>
<tr>
<td>Cd-N2</td>
<td>2.334(7)</td>
<td>Cd-N2-C6</td>
<td>173.2(6)</td>
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<tr>
<td>Cd-N3</td>
<td>2.323(7)</td>
<td>Cd-N3-C1</td>
<td>171.1(7)</td>
</tr>
<tr>
<td>Cd-N4</td>
<td>2.308(5)</td>
<td>Cd-N4-C2</td>
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<td>Cd-N5</td>
<td>2.283(7)</td>
<td>Cd-N5-C5</td>
<td>156.9(7)</td>
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<tr>
<td>Cd-N6</td>
<td>2.334(7)</td>
<td>Cd-N6-C3</td>
<td>152.3(7)</td>
</tr>
<tr>
<td>Cd-Cd (c axis)</td>
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<tr>
<td>Cd-Cd (α-β plane)</td>
<td>8.2661(5)</td>
<td>8.2938(5)</td>
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</table>
**Table S4.** Selected bond lengths and bond angles for the polymorph PII of our [TPrA]Cd[dca].

<table>
<thead>
<tr>
<th>bond length (Å)</th>
<th>Cd 390 K</th>
<th>bond angle (°)</th>
<th>Cd 390 K</th>
</tr>
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<tbody>
<tr>
<td>Cd-N1</td>
<td>2.30(1)</td>
<td>Cd-N1-C1</td>
<td>152(2)</td>
</tr>
<tr>
<td>Cd-N2</td>
<td>2.318(6)</td>
<td>Cd-N2-C2</td>
<td>172(1)</td>
</tr>
<tr>
<td>Cd-Cd (c axis)</td>
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<tr>
<td>Cd-Cd (α-b plane)</td>
<td>8.2539(7)</td>
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