Regulating Reversible Phase Transition Behaviors by poly-H/F Substitution in Hybrid Perovskite-like $2[\text{CH}_2\text{FCH}_2\text{NH}_3] \cdot [\text{CdCl}_4]$
Figure S2 simulated (red) and experimental (blue) powder XRD patterns of compound a) for 1, b) for 2 and c) for 3

Figure S3 the variable-temperature PXRD patterns of compound a) for 1, b) for 3

Figure S4 the TG-DTA (thermo gravimetric analysis and differential thermal analysis) curves of a) compound 1, b) 2 and c) 3 respectively
Figure S5 the two-dimensional sheet of a) 1-LTP and b) 1-HTP

Figure S6 the two-dimensional sheet of a) 2-LTP and b) 2-HTP

Figure S7 the two-dimensional sheet of a) 3-LTP and b) 3-HTP
Figure S8 a) the irregular framework of 3-LTP and b) the distorted square framework of 3-HTP

Figure S9 a) is the d$_{norm}$ surface picture of 1-LTP, b) and c) represents the exploded view of fingerprint for 1-LTP

Figure S10 a) is the d$_{norm}$ surface picture of 2-LTP, b) and c) represents the exploded view of fingerprint for 2-LTP
Figure S11 a) is the $d_{\text{norm}}$ surface picture of 3-LTP, b) and c) represents the exploded view of fingerprint 3-LTP

1. Table S1～S3

Table S1 the crystallographic data for 1–LTP and 1-HTP

| Compound | 1-LTP | 1-HTP |
|----------|-------|-------|
| Empirical formula | $\text{C}_4\text{H}_4\text{CdCl}_4\text{F}_2\text{N}_2$ | $\text{C}_4\text{H}_4\text{CdCl}_4\text{F}_2\text{N}_2$ |
| Formula weight | 382.37 | 372.29 |
| Temperature (K) | 270 | 300 |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | $Cmca$ |
| $a$ (Å) | 11.2047(8) | 7.4525(7) |
| $b$ (Å) | 7.6515(5) | 21.842(2) |
| $c$ (Å) | 7.3050(5) | 7.5766(6) |
| $V$ (Å$^3$) | 607.24(7) | 1233.29(19) |
| $Z$ | 2 | 4 |
| $D_{\text{acca}}$ / gm$^{-3}$ | 2.091 | 2.005 |
| $m$ (mm$^{-1}$) | 2.664 | 2.622 |
| $F(000)$ | 372.0 | 704.0 |
| Data / restraints / | 1070/0/62 | 744/0/47 |
| parameters | 2-LTP | 2-HTP |
|------------|-------|-------|
| GOF        | 1.142 | 1.078 |
| $R_1[I > 2\sigma(I)], wR_2$ (all data) | R1 = 0.0656, wR2 = 0.1861 | R1 = 0.0324, wR2 = 0.0898 |
| $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}} (\text{eÅ}^{-3})$ | 4.30/-1.14 | 0.57/-0.61 |

**Table S2** the crystallographic data for 2–LTP and 2-HTP

| Compound 2 | 2-LTP | 2-HTP |
|------------|-------|-------|
| Empirical formula | C₄H₁₂CdCl₄F₄N₂ | C₄H₁₂CdCl₄F₄N₂ |
| Formula weight | 418.36 | 418.36 |
| Temperature (K) | 293(2) | 340.01 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | P bca | C mca |
| $a$ (Å) | 7.5273(9) | 7.4610(7) |
| $b$ (Å) | 7.4027(9) | 23.412(2) |
| $c$ (Å) | 23.054(3) | 7.5566(7) |
| $V$ (Å³) | 1284.6(3) | 1320.0(2) |
| $Z$ | 4 | 4 |
| $D_{\text{acc}}$ / gm⁻³ | 2.163 | 2.105 |
| $m$ (mm⁻¹) | 2.550 | 2.482 |
| $F(000)$ | 808.0 | 808.0 |
| Data / restraints / parameters | 1462/0/71 | 806/51/55 |
| GOF | 1.396 | 1.207 |
|                | 3-LTP | 3-HTP |
|----------------|-------|-------|
| Empirical formula | $\text{C}_4\text{H}_{10}\text{CdCl}_4\text{F}_6\text{N}_2$ | $\text{C}_4\text{H}_{10}\text{CdCl}_4\text{F}_6\text{N}_2$ |
| Formula weight   | 454.34 | 454.34 |
| Temperature (K)  | 293    | 330.15 |
| Crystal system   | monoclinic | monoclinic |
| Space group      | $\text{C}2/c$ | $\text{P}2_1/c$ |
| $a$ (Å)          | 25.831(6) | 13.603(4) |
| $b$ (Å)          | 7.3258(17) | 7.435(3) |
| $c$ (Å)          | 7.3487(18) | 7.380(3) |
| $V$ (Å$^3$)      | 1390.6(6) | 718.4(5) |
| $Z$              | 4      | 2      |
| $D_{\text{acca}}$ (gm$^{-3}$) | 2.170 | 2.100 |
| $m$ (mm$^{-1}$)  | 2.385  | 2.309  |
| $F(000)$         | 872.0  | 436.0  |
| Data / restraints / parameters | 1648/0/79 | 1644/6/81 |
| GOF              | 1.149  | 1.126  |
| $R_1[I > 2\sigma(I)]$, $wR_2$ (all data) | $R1 = 0.0512$, $wR2 = 0.1196$ | $R1 = 0.0530$, $wR2 = 0.1423$ |
| $\Delta\rho_{\text{max}}$ / $\Delta\rho_{\text{min}}$ (eÅ$^{-3}$) | 1.04/-1.12 | 1.17/-0.87 |

**Table S3** the crystallographic data of 3–RTP and 3-HTP
|                  | 1-LTP            | 1-HTP            | 2-LTP            | 2-HTP            | 3-LTP            | 3-HTP            |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Cd1-Cl1          | 2.6574(15)       | Cd1-Cl1          | 2.6743(2)        |                  |                  |                  |
| Cd1-Cl1\(^1\)    | 2.6574(15)       | Cd1-Cl1\(^1\)    | 2.6743(2)        |                  |                  |                  |
| Cd1-Cl1\(^2\)    | 2.6787(15)       | Cd1-Cl1\(^2\)    | 2.6743(2)        |                  |                  |                  |
| Cd1-Cl1\(^3\)    | 2.6787(15)       | Cd1-Cl1\(^3\)    | 2.6743(2)        |                  |                  |                  |
| Cd1-Cl2          | 2.5318(17)       | Cd1-Cl2          | 2.5149(13)       |                  |                  |                  |
| Cd1-Cl2\(^1\)    | 2.5318(17)       | Cd1-Cl2\(^1\)    | 2.5148(14)       |                  |                  |                  |
| Cd1\(^4\)-Cl1    | 2.6787(15)       | Cd1\(^4\)-Cl1    | 2.6743(2)        |                  |                  |                  |
| Cd1-Cl1\(^4\)    | 2.5408(16)       |                  |                  |                  |                  |                  |
| Cd1-Cl1\(^5\)    | 2.5408(16)       |                  |                  |                  |                  |                  |
| Cl1-Cd1\(^4\)    | 2.6948(14)       |                  |                  |                  |                  |                  |

\(\Delta \rho_{\text{max}}/\Delta \rho_{\text{min}} (\text{eÅ}^{-3})\)  
1.59/-1.09  
2.62/-1.61
Table S5. Bond angles[^a] for 1, 2, 3.

|                  | 1-LTP       | 1-HTP       |
|------------------|-------------|-------------|
| Cl1-Cd1-Cl1      | 180.0       | Cl1-Cd1-Cl1 |
| Cl1-Cd1-Cl2      | 86.689(12)  | Cl1²-Cd1-Cl1³ | 180.0 |
| Cl1-Cd1-Cl3      | 93.311(12)  | Cl1-Cd1-Cl3  | 88.321(10) |
| Cl1³-Cd1-Cl1²    | 180.0       | Cl1¹-Cd1-Cl1² | 88.321(10) |
| Cl1¹-Cd1-Cl1²    | 93.311(12)  | Cl1¹-Cd1-Cl1² | 91.679(10) |
| Cl1¹-Cd1-Cl1³    | 86.689(12)  | Cl1¹-Cd1-Cl³  | 91.679(10) |
| Cl2¹-Cd1-Cl1     | 89.93(7)    | Cl2¹-Cd1-Cl³  | 89.55(4) |
| Cl2-Cd1-Cl1      | 90.07(7)    | Cl2-Cd1-Cl1  | 90.45(4) |
| Cl2-Cd1-Cl1¹     | 89.93(7)    | Cl2¹-Cd1-Cl¹  | 90.45(4) |
| Cl2¹-Cd1-Cl1¹    | 90.07(7)    | Cl2¹-Cd1-Cl1  | 89.55(4) |
| Cl2²-Cd1-Cl1²    | 88.78(6)    | Cl2¹-Cd1-Cl²  | 90.45(4) |
| Cl2¹-Cd1-Cl1³    | 88.78(6)    | Cl2-Cd1-Cl³   | 90.45(4) |
| Cl2²-Cd1-Cl1³    | 91.22(6)    | Cl2-Cd1-Cl³   | 89.55(4) |
| Cl2¹-Cd1-Cl1²    | 91.22(6)    | Cl2-Cd1-Cl²   | 89.55(4) |
| Cl2-Cd1-Cl2¹     | 180.00(10)  | Cl2-Cd1-Cl2¹  | 180.0 |

[^a]: Bond angles are in degrees.
| 2-LTP | 2-HTP | 3-LTP | 3-HTP |
|-------|-------|-------|-------|
| Cd1-Cd1-Cd1<sup>4</sup> | 164.82(10) | Cd1-Cd1-Cd1<sup>4</sup> | 166.91(7) |
| Cl1-Cd1-Cl1<sup>1</sup> | 180.0 | Cl2<sup>1</sup>-Cd1-Cl2 | 180.0 |
| Cl1-Cd1-Cl1<sup>2</sup> | 88.122(15) | Cl2-Cd1-Cl1<sup>1</sup> | 90.51(9) |
| Cl1-Cd1-Cl1<sup>3</sup> | 91.878(15) | Cl2<sup>1</sup>-Cd1-Cl1<sup>1</sup> | 90.50(9) |
| Cl1<sup>3</sup>-Cd1-Cl1<sup>2</sup> | 180.00(5) | Cl2-Cd1-Cl1<sup>1</sup> | 89.49(9) |
| Cl1<sup>1</sup>-Cd1-Cl1<sup>2</sup> | 91.878(15) | Cl2-Cd1-Cl1<sup>1</sup> | 90.50(9) |
| Cl1<sup>1</sup>-Cd1-Cl1<sup>3</sup> | 88.122(15) | Cl2<sup>1</sup>-Cd1-Cl1<sup>3</sup> | 90.50(9) |
| Cl2-Cd1-Cl1<sup>1</sup> | 89.43(5) | Cl2<sup>1</sup>-Cd1-Cl1<sup>2</sup> | 89.50(9) |
| Cl2<sup>1</sup>-Cd1-Cl1<sup>1</sup> | 90.57(5) | Cl2<sup>1</sup>-Cd1-Cl1<sup>1</sup> | 89.50(9) |
| Cl2<sup>1</sup>-Cd1-Cl1<sup>1</sup> | 90.57(5) | Cl1<sup>1</sup>-Cd1-Cl1<sup>2</sup> | 91.506(18) |
| Cl2<sup>1</sup>-Cd1-Cl1<sup>2</sup> | 88.69(5) | Cl1-Cd1-Cl1<sup>2</sup> | 88.494(18) |
| Cl2-Cd1-Cl1<sup>3</sup> | 88.69(5) | Cl1-Cd1-Cl1<sup>3</sup> | 91.506(18) |
| Cl2<sup>1</sup>-Cd1-Cl1<sup>3</sup> | 91.31(5) | Cl1<sup>1</sup>-Cd1-Cl1<sup>3</sup> | 88.494(18) |
| Cl2-Cd1-Cl1<sup>2</sup> | 91.31(5) | Cl1-Cd1-Cl1<sup>1</sup> | 180.0 |
| Cl2<sup>1</sup>-Cd1-Cl2 | 180.00(7) | Cl2<sup>1</sup>-Cd1-Cl1<sup>3</sup> | 180.00(14) |
| Cd1-Cd1-Cd1<sup>4</sup> | 158.12(7) | Cd1<sup>4</sup>-Cd1-Cd1 | 166.55(14) |
| Cl2-Cd1-Cl2<sup>1</sup> | 180.0 | Cl1<sup>1</sup>-Cd1-Cl1 | 180.0 |
| Cl2-Cd1-Cl2<sup>2</sup> | 90.60(2) | Cl1-Cd1-Cl2<sup>1</sup> | 88.53(12) |
| Cl2-Cd1-Cl2<sup>3</sup> | 89.40(2) | Cl1-Cd1-Cl2<sup>2</sup> | 91.47(12) |
| Cl2<sup>3</sup>-Cd1-Cl2<sup>2</sup> | 180.0 | Cl1-Cd1-Cl2<sup>1</sup> | 90.76(13) |
| Cl2<sup>1</sup>-Cd1-Cl2<sup>2</sup> | 89.40(2) | Cl1-Cd1-Cl2 | 89.24(13) |
3. Calculation of the $\Delta S_1$ and N value for compounds in the heating and cooling cycles

Compound 1

① Calculation of $\Delta S_1$ and $N$ in the cooling cycle

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T_C}$$

$$= \frac{18.00 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{291.75 \text{ K}}$$

$$= 28.532 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_1 = R \ln N_1$$

$$N_1 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{28.532 \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}\right)$$

$$= 30.933$$
Calculation of $\Delta S_1$ and $N$ in the heating cycle

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T}$$

$$= \frac{17.16 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{292.78 \text{ K}}$$

$$= 27.105 \text{ J mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_2 = R \ln N_2$$

$$N_2^2 = \exp \left( \frac{\Delta S_2}{R} \right) = \exp \left( \frac{27.105 \text{ J mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}} \right)$$

$$= 26.054$$

Compound 2

Calculation of $\Delta S_1$ and $N$ in the cooling cycle

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T}$$

$$= \frac{26.65 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{318.48 \text{ K}}$$

$$= 38.698 \text{ J mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_1 = R \ln N_1$$

$$N_1 = \exp \left( \frac{\Delta S_1}{R} \right) = \exp \left( \frac{38.698 \text{ J mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}} \right)$$

$$= 105.064$$

Calculation of $\Delta S_1$ and $N$ in the heating cycle

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$
\[ \approx \frac{\Delta H}{T} \]

\[ = \frac{24.16 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{317.63 \text{ K}} \]

\[ = 35.176 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ \Delta S_2 = R \ln N_2 \]

\[ N_2 = \exp \left( \frac{\Delta S_2}{R} \right) = \exp \left( \frac{23.377 \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \right) \]

\[ = 68.783 \]

Compound 3

Calculation of \( \Delta S_1 \) and \( N \) in the cooling cycle

\[ \Delta S_1 = \int_{T_1}^{T_2} \frac{Q}{T} dT \]

\[ \approx \frac{\Delta H}{T} \]

\[ = \frac{17.70 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{325.80 \text{ K}} \]

\[ = 25.124 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ \Delta S_1 = R \ln N_1 \]

\[ N_1 = \exp \left( \frac{\Delta S_1}{R} \right) = \exp \left( \frac{25.124 \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \right) \]

\[ = 20.531 \]

Calculation of \( \Delta S_1 \) and \( N \) in the heating cycle

\[ \Delta S_2 = \int_{T_1}^{T_2} \frac{Q}{T} dT \]

\[ \approx \frac{\Delta H}{T} \]

\[ = \frac{17.78 \text{ J g}^{-1} \times 462.46 \text{ g mol}^{-1}}{327.32 \text{ K}} \]
\[ \Delta S_2 = R \ln N_2 \]

\[ N_2 = \exp \left( \frac{\Delta S^2}{R} \right) = \exp \left( \frac{5.945 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}} \right) \]

\[ = 20.522 \]