Supporting Information

Two-dimensional organic-inorganic hybrid perovskite ferroelastics: $(PEA)_2[CdCl_4]$, $(3\text{-}FPEA)_2[CdCl_4]$, and $(4\text{-}FPEA)_2[CdCl_4]$

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Experimental

Sample preparation. Compound **1** was obtained as crystalline samples from a methanol/water ($V_{methanol}$: V_{water} = 1 : 1) solution containing with a molar ratio of PEA : Cd equal to 2 at room temperature over two weeks, totally different from the earlier reported method (S. Kassoul, A. Kaiba, P. Guionneau and A. Belaaraj, *J. Struct. Chem.*, **2016**, *57*, 737−743). Compounds **2**−**3** were prepared by using the same method as compound **1**.

General Measurements. Differential scanning calorimetry measurements were carried out on the DSC214 Polyma instrument in the whole measured temperature range 293−463K with the rate of 20 K min^{-1} at atmospheric pressure in aluminum crucibles. For dielectric measurements, the polycrystalline samples were used as the plates with thickness of around 0.5 mm and area of around 9mm^2. Carbon conducting paste deposited on the plate surfaces was used as electrodes. A Tonghui TH2828A impedance analyzer was used to measure the dielectric constants. The applied electric field in the measurements was 1 V. The ferroelastic domain observations were detected with an Olympus BX51TRF optical polarizing microscope. The temperature remained stable with an accuracy of 0.2 K by using an INSTEC HCC602 cooling/heating stage. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku D/MAX 2000 PC X-ray diffractometer. And the X-ray wavelength is 0.15406 nm.

X-ray diffraction experiments.

Various-temperature single-crystal diffraction data were collected on a Rigaku synergy diffractometer using Mo-K_α (λ= 0.71073 Å) radiation from a graphite monochromator equipped with gas spray cooler device. The crystal structures were resolved by direct method and then refined by full-matrix least-square method based on F^2 using the OLEX2 software package. At low-temperature phase, all non-hydrogen atoms were refined anisotropically and located in difference Fourier maps. And the positions of all hydrogen atoms were generated geometrically with U_{iso} = 1.2 U_{eq} (C and N). The organic amine is disordered with not all H atoms allowed for compound **2**. At high-temperature phase, the space groups were chosen according to the Aizu principle. The organic cations were not modeled according to it chemical sense, because of the highly disordered form at high-temperature phase. Besides, the organic fluoro-amine is disordered with no H atoms allowed for in the model.

Supplemental Figures

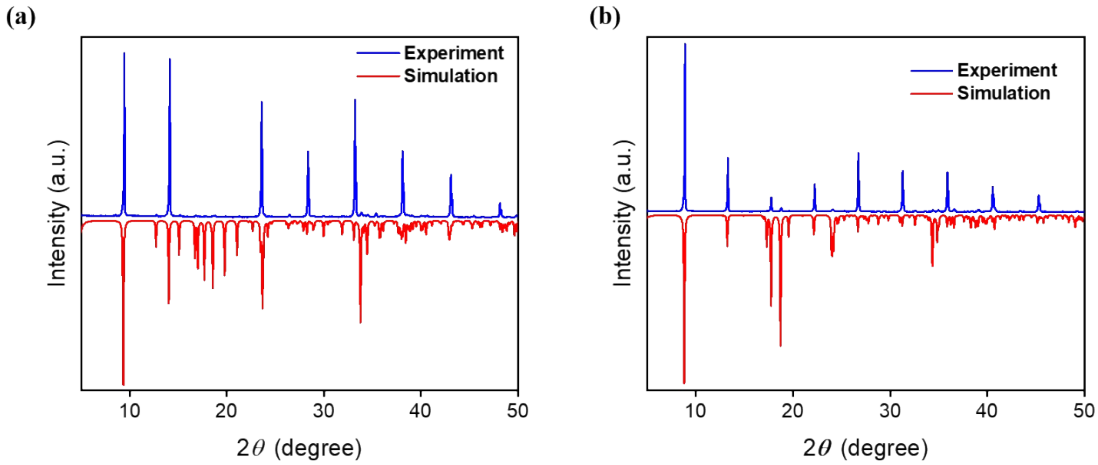
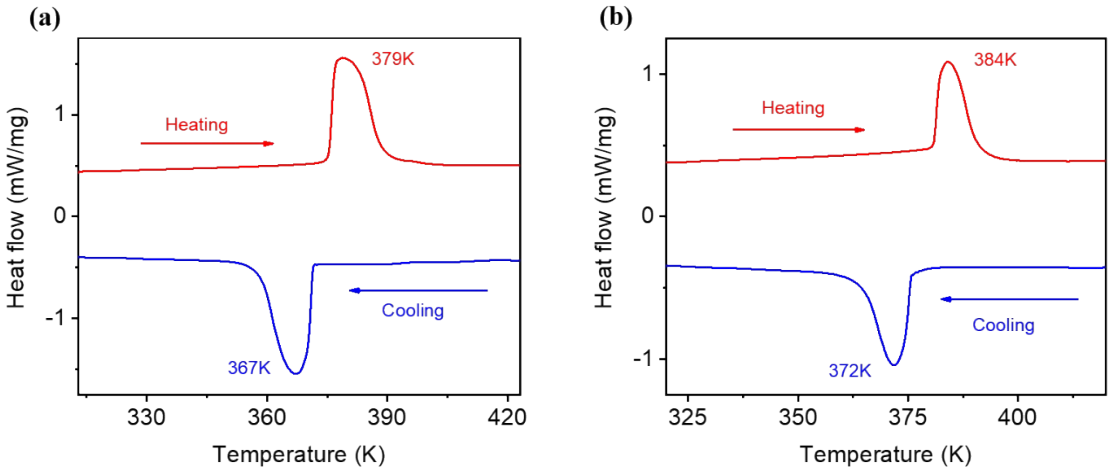


Figure S1. PXRD patterns of **2** and **3** at 293 K, respectively.



FigureS2. (a) DSC curves of **2**, (b) DSC curves of **3**.

Hirshfeld surface analysis

In order to study the interaction between PEA and the anion layer more comprehensively, we performed Hirshfeld surface analysis on 1 to obtain its interaction visualization map and fingerprint map (Fig. S3). The interaction force of 1 in LTP is mainly composed of blue and white, which means that the overall arrangement of cations is relatively loose (Fig. S3a). The red part in the surface plot represents the hydrogen bond formed between the PEA cation and the anion framework. The strong N−H···Cl hydrogen bonding between PEA and the anion layer formed a red area on the interaction map, and the [H···Cl] 2D fingerprint was a strong 23.2% (Fig. S3c). Among them, the interaction 2D fingerprints of [H···C] and [C···H] occupy 54.7% and 12.4%, respectively, which means that the interaction force between cations is mainly composed of H···H and C···H (Fig.S3b, S3d). Similar to the stacking of **1**, the fingerprints of **3** is presented in Fig. S4. Since **2** is 2-fold disorder at 293K, Hirshfeld surface analysis is not performed.

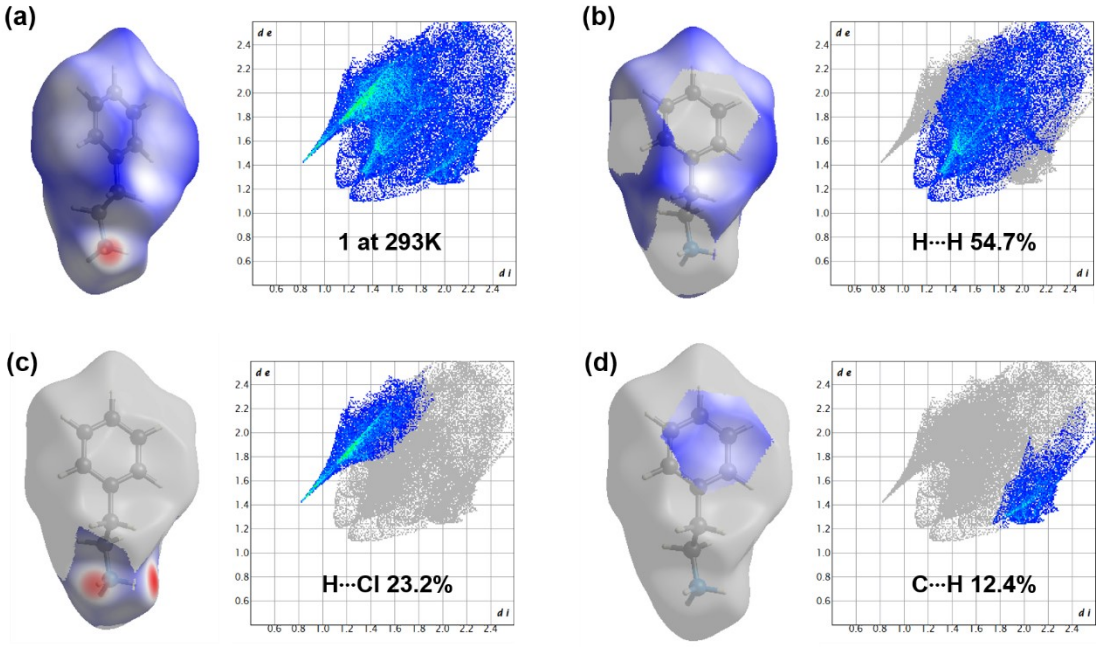


Figure S3 (a) Visualization map of the interaction force and fingerprint of compound **1** at 293K. (b) (c) (d)Visualization map of the interaction and the ratio of [H···H] [H···Cl] and [C···H].

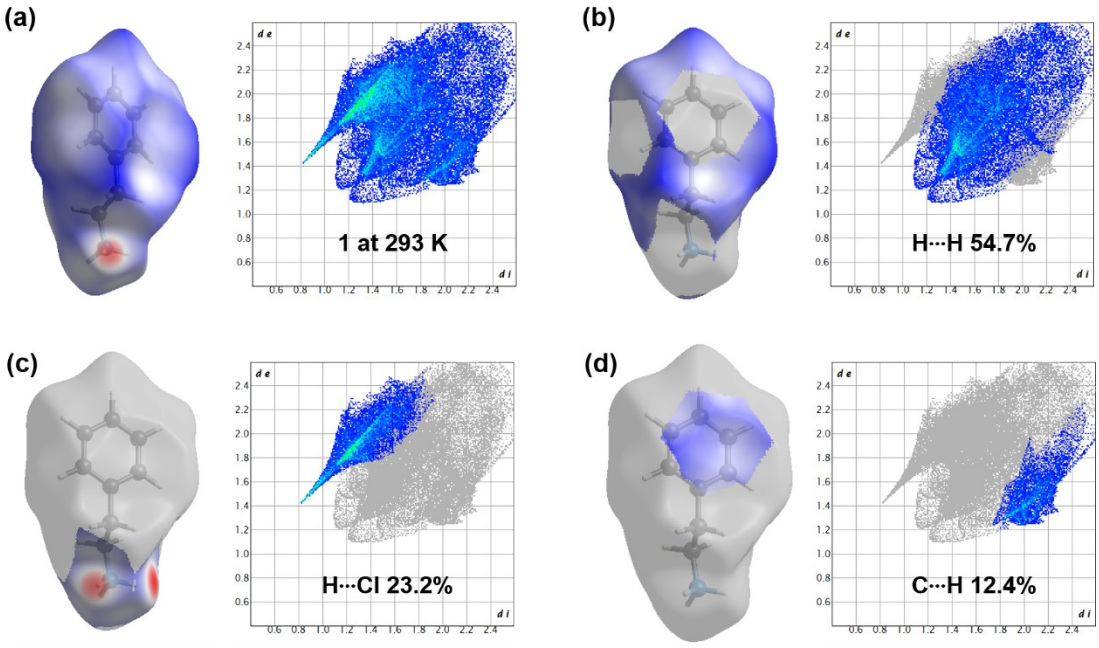


Figure S4 (a) Visualization map of the interaction force and fingerprint of compound **3** at 293K. (b), (c), (d) Visualization map of the interaction and the ratio of [H···Cl] [C···H] and [F···H].

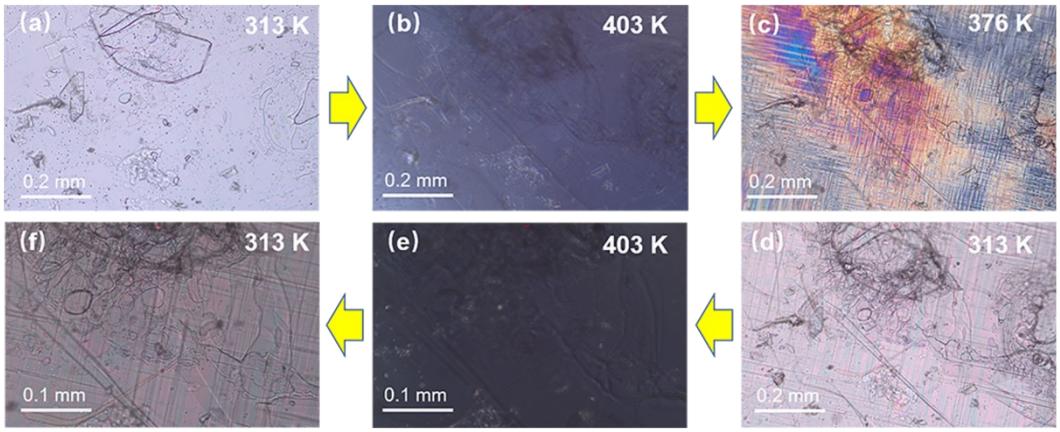


Figure S5 (a) The crystal morphology of **2** at 313 K. (b), (c), (d), (e), and (f) The observations of temperature dependent evolution of the ferroelastic domain structures of **2** by polarized microscopy.

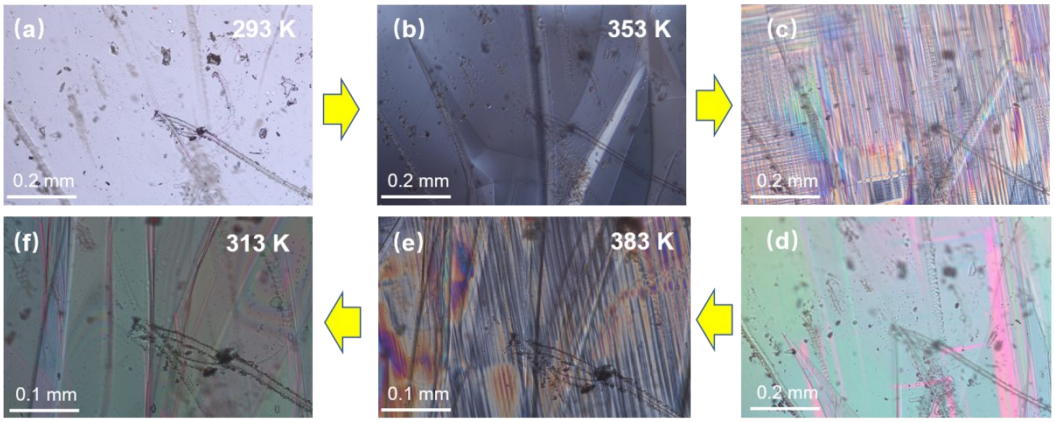


Figure S6 (a) The crystal morphology of **3** at 313 K. (b), (c), (d), (e), and (f) The observations of temperature dependent evolution of the ferroelastic domain structures of **3** by polarized microscopy.

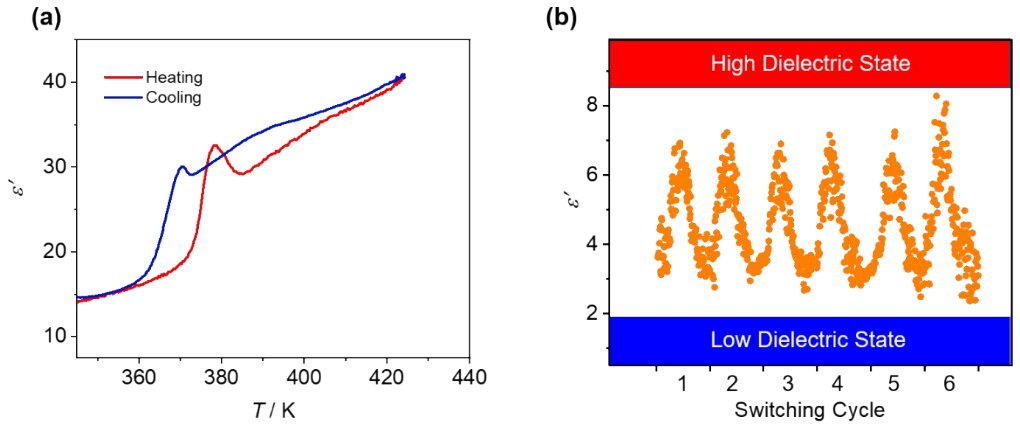


Figure S7. (a) Dielectric diagrams of **2** at 500Hz. (b) Dielectric constant-switching traces of **2** at 100 Hz and variable temperature. After six cycles, the value of ε' shows no obvious changes indicating a highly switchable reversibility of ε'.

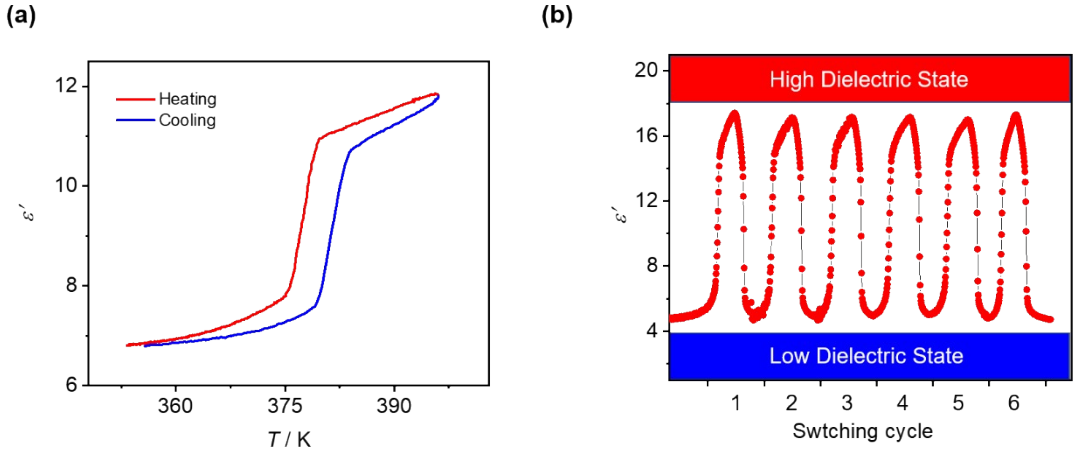


Figure S8. (a) Dielectric diagrams of **3** at 500 Hz. (b) Dielectric constant-switching traces of **3** at 750 Hz and variable temperature. After six cycles, the value of ε' shows no obvious changes indicating a highly switchable reversibility of ε'.

Supplemental Tables

TableS1. Crystal Data and Structure Refinement Details for **2** at 293 K and 403 K.

T / *K*	293K	403K
Formula weight	512.39	512.39
Empirical formula	$C_{16}CdCl_4F_2N_2$	$C_{16}CdCl_4F_2N_2$
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$I4/mmm$
a / Å	19.0475(14)	5.3186(4)
b / Å	7.4870(5)	5.3186(4)
c / Å	7.5538(5)	40.261(8)

α / °	90	90
β / °	96.033(6)	90
γ / °	90	90
V / Å^3	1071.27(13)	1138.9(3)
Z	2	2
D_{calc} / g·cm^{-3}	1.589	1.494
μ / mm^{-1}	1.534	1.443
F(000)	488	488.0
2θ *range* / °	4.3−62.066	4.046−61.436
Reflns collected	8469	2465
Independent reflns (R_{int})	3432 (0.0595)	614(0.0444)
No. of parameters	157	81
R_1[a], wR_2[b] [I>2σ(I)]	0.0959, 0.2710	0.0483, 0.1316
R_1, wR_2 [all data]	0.1095, 0.2856	0.0525, 0.1353
GOF	1.149	1.138
$\Delta\rho$[c] / e·Å^{-3}	7.74, −2.45	0.60, −0.53
CCDC	2204247	2204248

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$; [c] maximum and minimum residual electron density.

TableS2. Crystal Data and Structure Refinement Details for **3** at 293K and 408 K

T / *K*	293K	408K
Formula weight	534.57	512.39
Empirical formula	$C_{16}H_{22}CdCl_4F_2N_2$	$C_{16}CdCl_4F_2N_2$
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$I4/mmm$
a / Å	20.0721(17)	5.2977(2)
b / Å	7.3523(6)	5.2977(2)
c / Å	7.4427(5)	40.592(3)
α / °	90	90
β / °	94.274(7)	90
γ / °	90	90
V / Å^3	1095.31(15)	1139.23(11)
Z	2	2

D_{calc} / g·cm^{-3}	1.621	1.494
μ / mm^{-1}	1.503	1.443
F(000)	532.0	488.0
2θ *range* / °	4.07−62.068	4.014−61.586
Reflns collected	10742	5062
Independent reflns (R_{int})	3498 (0.0711)	618(0.0231)
No. of parameters	116	78
R_1[a], wR_2[b] [I>2σ(I)]	0.0419, 0.1071	0.0516, 0.1385
R_1, wR_2 [all data]	0.0514, 0.1133	0.0520, 0.1393
GOF	0.993	1.270
$\Delta\rho$[c] / e·Å^{-3}	0.93, −1.15	0.65, −0.69
CCDC	2204251	2204252

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$; [c] maximum and minimum residual electron density.

Table S3 Selected bond lengths [Å] and angles [°] for **1** at 293 K and 403 K.

293K			
Cd1–Cl2	2.6516(9)	Cl3^3–Cd1–Cl2^2	89.96(4)
Cd1–Cl2^1	2.6497(9)	Cl3–Cd1–Cl2	88.01(3)
Cd1–Cl2^2	2.6516(9)	Cl3–Cd1–Cl2^3	91.99(3)
Cd1–Cl2^3	2.6497(9)	Cl3^3–Cd1–Cl2	91.99(3)
Cd1–Cl3^2	2.5549(11)	Cl3^3–Cd1–Cl2^1	90.04(4)
Cd1–Cl3	2.5551(11)	Cl3–Cd1–Cl2^2	90.04(4)
N1–C3	1.484(7)	Cl3^3–Cd1–Cl2^3	88.01(3)
C2–C5	1.377(8)	Cl3–Cd1–Cl2^1	89.96(4)
C2–C6	1.511(8)	Cl3^3–Cd1–Cl3	180.0
C2–C7	1.368(8)	Cd1^4–Cl2–Cd1	162.32(5)
C3–C6	1.496(7)	C5–C2–C6	122.0(5)
C4–C5	1.386(8)	C7–C2–C5	117.2(6)
C4–C8	1.334(10)	C7–C2–C6	120.8(5)
C7–C9	1.393(8)	N1–C3–C6	111.0(4)

C8–C9	1.326(10)	C8–C4–C5	121.3(6)
$Cl2^{1}$–Cd1–$Cl2^{2}$	180.00(6)	C2–C5–C4	120.3(6)
$Cl2^{2}$–Cd1–$Cl2^{3}$	89.697(9)	C3–C6–C2	113.3(5)
Cl21–Cd1–Cl23	90.303(9)	C2–C7–C9	120.6(6))
$Cl2^{3}$–Cd1–Cl2	180.0	C9–C8–C4	119.4(6)
$Cl2^{1}$–Cd1–Cl2	89.697(9)	C8–C9–C7	121.1(7)
$Cl2^{2}$–Cd1–Cl2	90.303(9)		

^{1}1/2 - *x*, -1/2+*y*, +*z*; ^{2}1-*x*, -*y*, -*z*; ^{3}1/2+*x*,1/2-*y*, -*z*

^{1}1/2 - *x*, -1/2+*y*, +*z*; ^{2}1/2+*x*,1/2-*y*, -*z*; ^{3}1-*x*, -*y*, -*z*; ^{4}-1/2+*x*,1/2-*y*, -*z*

403K

Cd1–$Cd1^{1}$	0.305(10)	Cl1–Cd1–$Cl1^{3}$	89.812(13)
Cd1–$Cl1^{2}$	2.6589(3)	$Cl1^{2}$–Cd1–$Cl1^{3}$	173.4(2)
Cd1–$Cl1^{3}$	2.6589(3)	$Cl1^{3}$–Cd1–$Cl2^{1}$	86.72(11)
Cd1–$Cl1^{4}$	2.6589(3)	Cl1–Cd1–$Cl2^{1}$	86.72(11)
Cd1–Cl1	2.6589(3)	$Cl1^{4}$–Cd1–$Cl2^{1}$	86.72(11)
Cd1–Cl2	2.358(6)	$Cl1^{2}$–Cd1–$Cl2^{1}$	86.72(11)
Cd1–$Cl2^{1}$	2.663(6)	Cl2–Cd1–$Cl1^{3}$	93.28(11)
N1–C6	1.41(5)	Cl2–Cd1–$Cl1^{4}$	93.28(11)
C1–C4	1.51(3)	Cl2–Cd1–Cl1	93.28(11)
C1–C6	1.52(5)	Cl2–Cd1–$Cl1^{2}$	93.28(11)
C4–C2	1.40(7)	Cl2–Cd1–$Cl2^{1}$	180.0
C3–C5	1.27(6)	Cd1–Cl1–$Cd1^{5}$	173.4(2)
C2–C5	1.64(5)	Cd1–Cl1–$Cd1^{6}$	180.0
$Cd1^{1}$–Cd1–$Cl1^{2}$	86.72(11)	Cd1–Cl1–$Cd1^{1}$	6.6(2)
$Cd1^{1}$–Cd1–Cl1	86.72(11)	$Cd1^{1}$–Cl1–$Cd1^{5}$	180.0(2)
$Cd1^{1}$–Cd1–$Cl1^{3}$	86.72(11)	$Cd1^{1}$–Cl1–$Cd1^{6}$	173.4(2)
$Cd1^{1}$–Cd1–$Cl1^{4}$	86.72(11)	$Cd1^{5}$–Cl1–$Cd1^{6}$	6.6(2)
$Cd1^{1}$–Cd1–$Cl2^{1}$	0.000(3)	Cd1–Cl2–$Cd1^{1}$	180.0
$Cd1^{1}$–Cd1–Cl2	180.0	C4–C1–C6	113(2)
$Cl1^{2}$–Cd1–$Cl1^{4}$	89.812(13)	C2–C4–C1	125(5)
$Cl1^{4}$–Cd1–Cl1	173.4(2)	N1–C6–C1	124(4)
$Cl1^{2}$–Cd1–Cl1	89.812(13)	C4–C2–C5	126(3)

Cl1[4]–Cd1–Cl1[3]	89.812(13)	C3–C5–C2	100(3)

[1]2 - *x*,2-*y*,1-*z*; [2]2-*y*, +*x*, +*z*; [3]2-*y*,1+*x*, +*z*; [4]1+*x*, +*y*, +*z*

[1]2 - *x*,2-*y*,1-*z*; [2]2-*y*,1+*x*, +*z*; [3]2-*y*, +*x*, +*z*; [4]1+*x*, +*y*, +*z*; [5]-1+*x*, +*y*, +*z*; [6]1-*x*,2-*y*,1-*z*

Table S4. Bond lengths [Å] and bond angles [°] of the hydrogen bond at 293 K of **1**.

D − H···A	D − H	H···A	D···A	DHA
N1 − H1A···Cl2[1]	0.89	2.37	3.246(4)	169
N1 − H1B···Cl3	0.89	2.43	3.278(4)	160
N1 − H1C···Cl3[2]	0.89	2.58	3.432(4)	160

Symmetry codes: (1) 1+*x*, *y*, *z*; (2) 3/2-*x*, -1/2+*y*, *z*.

Table S4 Selected bond lengths [Å] and angles [°] for **2** at 293 K and 403 K.

293K			
Cd1–Cl2[1]	2.6747(17)	Cl2[1]–Cd1–Cl2[3]	89.770(14)
Cd1–Cl2[2]	2.6774(17)	Cl2[3]–Cd1–Cl2[2]	180.00(11)
Cd1–Cl2[3]	2.6774(17)	Cl1–Cd1–Cl2[2]	90.49(8)
Cd1–Cl2	2.6747(17)	Cl1[1]–Cd1–Cl1	180.0
Cd1–Cl1	2.535(2)	Cd1–Cl2–Cd1[4]	167.02(11)
Cd1–Cl1[1]	2.535(2)	C6–C4–C5	120.0
N1–C2	1.363(18)	C6–C4–C3	119.2(14)
C4–C6	1.3900	C6–C4–C1	102.0(15)
C4–C5	1.3900	C5–C4–C3	120.4(14)
C4–C3	1.60(3)	C5–C4–C1	121.9(15)
C4–C1	1.60(3)	C3–C4–C1	48(2)
C4–C7	1.27(4)	C7–C4–C6	26(2)
C6–C10	1.3900	C7–C4–C5	123(2)
C10–C12	1.3900	C7–C4–C3	107(2)
C12–C8	1.3900	C7–C4–C1	112(2)
C8–C5	1.3900	C10–C6–C4	120.0
C8–F2	1.29(2)	C6–C10–C12	120.0

C5–C9	1.36(4)	C8–C12–C10	120.0
C2–C3	1.32(4)	C12–C8–C5	120.0
C2–C1	1.31(4)	F2–C8–C12	121.3(17)
C7–C11	1.43(5)	F2–C8–C5	118.7(17)
F1–C9	1.32(4)	C8–C5–C4	120.0
C9–C13	1.25(5)	C9–C5–C4	115(2)
C13–C11	1.33(5)	C9–C5–C8	35.0(14)
$Cl2^1$–Cd1–Cl2	180.0	C3–C2–N1	133(2)
$Cl2^1$–Cd1–$Cl2^2$	90.230(13)	C1–C2–N1	136(2)
Cl2–Cd1–$Cl2^2$	89.770(13)	C1–C2–C3	60(2)
Cl2–Cd1–$Cl2^3$	90.230(13)	C2–C3–C4	115(3)
Cl1–Cd1–$Cl2^1$	89.65(8)	C2–C1–C4	115(3)
$Cl1^1$–Cd1–$Cl2^1$	90.35(8)	C4–C7–C11	116(3)
$Cl1^1$–Cd1–Cl2	89.65(8)	F1–C9–C5	113(3)
Cl1–Cd1–Cl2	90.35(8)	C13–C9–C5	125(4)
$Cl1^1$–Cd1–$Cl2^2$	89.51(8)	C13–C9–F1	121(4)
Cl1–Cd1–$Cl2^3$	89.51(8)	C9–C13–C11	118(4)
$Cl1^1$–Cd1–$Cl2^3$	90.49(8)	C13–C11–C7	121(4)

^{1}1 - *x*, -*y*,1-*z*; ^{2}1-*x*, -1/2+*y*,1/2-*z*; ^{3}+*x*,1/2-*y*,1/2+*z* ^{1}1 - *x*, -*y*,1-*z*; ^{2}+*x*,1/2-*y*,1/2+*z*; ^{3}1-*x*, -1/2+*y*,1/2-*z*; ^{4}1-*x*,1/2+*y*,1/2-*z*

403K

Cd1–Cl2	2.6593(2)	Cl1–Cd1–$Cl2^2$	90.0
Cd1–$Cl2^1$	2.6593(2)	$Cl1^4$–Cd1–Cl2	90.0
Cd1–$Cl2^2$	2.6593(2)	Cl1–Cd1–$Cl2^1$	90.0
Cd1–$Cl2^3$	2.6593(2)	Cl1–Cd1–Cl2	90.0
Cd1–Cl1	2.510(4)	$Cl1^4$–Cd1–$Cl2^2$	90.0
Cd1–$Cl1^4$	2.510(4)	Cl1–Cd1–$Cl2^3$	90.0
N1–C8	1.4801(11)	$Cl1^4$–Cd1–$Cl2^1$	90.0
C8–C7	1.4797(12)	$Cl1^4$–Cd1–$Cl2^3$	90.0
C7–C6	1.4795(11)	$Cl1^4$–Cd1–Cl1	180.0
C1–C2	1.3900	$Cd1^5$–Cl2–Cd1	180.0
C1–C6	1.3900	C7–C8–N1	102.02(10)

C2–C3	1.3900	C6–C7–C8	102.05(11)
C2–F1	1.31(2)	C2–C1–C6	120.0
C3–C4	1.3900	C3–C2–C1	120.0
C4–C5	1.3900	F1–C2–C1	100(3)
C5–C6	1.3900	F1–C2–C3	140(3)
Cl2–Cd1–Cl2[1]	180.0	C2–C3–C4	120.0
Cl2[2]–Cd1–Cl2[3]	180.0	C5–C4–C3	120.0
Cl2–Cd1–Cl2[3]	90.0	C6–C5–C4	120.0
Cl2[1]–Cd1–Cl2[2]	90.0	C1–C6–C7	118.3(11)
Cl2–Cd1–Cl2[2]	90.0	C5–C6–C7	119.7(12)
Cl2[1]–Cd1–Cl2[3]	90.0	C5–C6–C1	120.0

[1]2 - *y*, +*x*, +*z*; [2]2-*y*,1+*x*, +*z*; [3]1+*x*, +*y*, +*z*; [4]2-*x*,2-*y*,1-*z* ;[1]1 + *x*, +*y*, +*z*; [2]2-*y*, +*x*, +*z*; [3]2-*y*,1+*x*, +*z*; [4]2-*x*,2-*y*,1-*z*; [5]-1+*x*, +*y*, +*z*

Table S5 Selected bond lengths [Å] and angles [°] for **3** at 293 K and 408 K.

293K			
Cd1–Cl2[1]	2.6483(6)	Cl3[1]–Cd1–Cl2[3]	89.89(3)
Cd1–Cl2	2.6457(6)	Cl3–Cd1–Cl2	91.95(3)
Cd1–Cl2[2]	2.6483(6)	Cl3[1]–Cd1–Cl2[1]	91.95(3)
Cd1–Cl2[3]	2.6457(6)	Cl3[1]–Cd1–Cl2	88.05(3)
Cd1–Cl3	2.5534(8)	Cl3–Cd1–Cl2[2]	89.89(3)
Cd1–Cl3[3]	2.5534(8)	Cl3–Cd1–Cl2[3]	90.11(3)
N12–C11	1.482(5)	Cl3–Cd1–Cl2[1]	88.05(3)
C11–C10	1.502(6)	Cl3[1]–Cd1–Cl2[2]	90.11(3)
C4–C10	1.503(7)	Cl3–Cd1–Cl3[1]	180.0
C4–C9	1.372(7)	Cd1–Cl2–Cd1[4]	162.29(4)
C4–C5	1.370(6)	N1[2]–C11–C10	111.1(3)
F13–C7	1.369(6)	C9–C4–C10	122.3(4)
C9–C8	1.364(7)	C5–C4–C10	121.5(4)
C7–C8	1.321(8)	C5–C4–C9	116.3(5)
C7–C6	1.327(8)	C11–C10–C4	112.5(4)
C5–C6	1.379(6)	C8–C9–C4	122.2(5)
Cl2–Cd1–Cl2[1]	180.0	C8–C7–F13	118.8(6)

Cl2^{2}–Cd1–Cl2^{3}	180.0	C8–C7–C6	121.6(5)
Cl2–Cd1–Cl2^{3}	89.918(7)	C6–C7–F13	119.6(5)
Cl2^{1}–Cd1–Cl2^{2}	89.918(8)	C7–C8–C9	119.3(5)
Cl2–Cd1–Cl2^{2}	90.082(7)	C4–C5–C6	120.8(5)
Cl2^{1}–Cd1–Cl2^{3}	90.082(8)	C7–C6–C5	119.9(5)

^{1}+*x*, 3/2-*y*, 1/2+*z*; ^{2}1 - *x*, 1/2+*y*, 1/2-*z*; ^{3}1-*x*, 2-*y*, 1-*z*; ^{1}1 - *x*, 2-*y*,1-*z*; ^{2}1-*x*,1/2+*y*,1/2-*z*; ^{3}+*x*,3/2-*y*,1/2+*z*; ^{4}1-*x*, -1/2+*y*,1/2-*z*

408K

Cd1–Cl2	2.64885(10)	Cl2^{1}–Cd1–Cl2^{3}	90.0
Cd1–Cl2^{1}	2.64885(10)	Cl1–Cd1–Cl2^{3}	90.0
Cd1–Cl2^{2}	2.64885(10)	Cl1–Cd1–Cl2^{2}	90.0
Cd1–Cl2^{3}	2.64885(10)	Cl1^{4}–Cd1–Cl2^{1}	90.0
Cd1–Cl1^{4}	2.511(3)	Cl1^{4}–Cd1–Cl2	90.0
Cd1–Cl1	2.510(3)	Cl1^{4}–Cd1–Cl2^{2}	90.0
C6–N1	1.45(4)	Cl1^{4}–Cd1–Cl2^{3}	90.0
C6–C5	1.43(4)	Cl1–Cd1–Cl2^{1}	90.0
C4–C5	1.56(4)	Cl1–Cd1–Cl2	90.0
C4–C3	1.39(5)	Cl1–Cd1–Cl1^{4}	180.0
C1–F1	1.60(5)	Cd1^{5}–Cl2–Cd1	180.0
C1–C2	1.41(2)	C5–C6–N1	119(6)
C2–C3	1.44(2)	C3–C4–C5	115(4)
Cl2–Cd1–Cl2^{1}	180.0	C2–C1–F1	133(4)
Cl2^{2}–Cd1–Cl2^{3}	180.0	C1–C2–C3	110(3)
Cl2–Cd1–Cl2^{3}	90.0	C6–C5–C4	115(4)
Cl2^{1}–Cd1–Cl2^{2}	90.0	C4–C3–C2	112(3)
Cl2–Cd1–Cl2^{2}	90.0		

^{1}+*x*, 1+*y*,+*z*; ^{2}2-*y*, +*x*, +*z*; ^{3}1 - *y*, +*x*, +*z*; ^{4}2-*x*,2-*y*,1-*z*; ^{1}+*x*,1+*y*, +*z*; ^{2}1-*y*, +*x*, +*z*; ^{3}2-*y*, +*x*, +*z*; ^{4}2-*x*,2-*y*,1-*z*; ^{5}+*x*, -1+*y*, +*z*

Table S7 Bond lengths [Å] and bond angles [°] of the hydrogen bond at 293 K of **3**.

D − H···A	D − H	H...A	D...A	DHA
N12 − H12A···Cl2	0.89	2.37	3.253(3)	171
N12 − H12B···Cl3^{2}	0.89	2.41	3.271(2)	162
N12 − H12C···Cl3^{1}	0.89	2.58	3.425(4)	158

Symmetry codes: (1) 1-*x*, -1/2+*y*, 3/2-*z*; (2) 1-*x*, 1-*y*, 1-*z*.