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Supporting Information

Metal Regulated Organic–Inorganic Hybrid Ferroelastic Materials: $[(CH_3)_3CN(CH_3)_2CH_2F]_2[MBr_4]$ (M = Cd and Zn)

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EXPERIMENTAL SECTION

Synthesis. To synthesize Dimethyl-(tert-butyl)-fluoro-methyl-ammonium bromide, N, N-Dimethyl-tert-butylamine (4.048 g, 40 mmol) and fluorobromomethane (4.517 g, 40 mmol) were added to in dichloromethane (50.0 mL) in an ice-water bath. Then, the mixture was stirred continuously at room temperature for 4 hours. After suction filtration the resulting white precipitates were washed three times with ethyl acetate (yield=60%). The purity of product was improved by recrystallization with ethanol/ethyl (1/10) and was confirmed by the mass spectrum with liquid chromatography/time-of-flight mass spectrometry.

The equimolar mixture of **[**$(CH_3)_3CN(CH_3)_2CH_2F$**]**Br and $CdBr_2 \cdot 4H_2O$ was dissolved in deionized water. This mixture was stirred till becoming clear and then was evaporated at room temperature. After 3 weeks of slow evaporation, colorless strip-like crystals of **[**$(CH_3)_3CN(CH_3)_2CH_2F$**]**$_2$**[**$CdBr_4$**]** **(1)** were obtained. Similarly, colorless strip-like crystals of **[**$(CH_3)_3CN(CH_3)_2CH_2F$**]**$_2$**[**$ZnBr_4$**]** (**2**) were grown by the slow evaporation of the aqueous solution containing equimolar **[**$(CH_3)_3CN(CH_3)_2CH_2F$**]**Br and $ZnBr_2$ at room temperature. For compounds **1** and **2**, the toxicity of cadmium and zinc should be noted owing to the organic-inorganic hybrid material. The solubility of **1** is 18.6 g/100 mL water at 20 °C and the solubility of **2** is 46.3 g/100 mL at 20 °C.

Characterizations.

IR Spectrum Measurement

IR spectral measurements were performed on KBr diluted pellets of compounds **1** and **2** at room temperature using a Shimadzu model IR-60 spectrometer.

Powder X-ray Diffraction

The powder X-ray diffraction (PXRD) data for compounds **1** and **2** were measured on a PANalytical X'Pert PRO X-Ray Diffractometer at 293 K. Diffraction patterns were collected in the 2θ range of 5–50° with a step size of 0.02°.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of compound **1** and **2** were performed on a Netzsch Model TG 209F1 instrument. The measurements were collected in nitrogen flow from 305 K to 1000 K, and the results show that both compounds **1** and **2** begin to decompose at 410 K.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) of compounds **1** and **2** were measured on PerkinElmer Diamond DSC instrument that 25.6 mg (**1**) and 13.6 mg (**2**) powder samples were placed in aluminum crucibles with heating and cooling rates of 20 K/min under nitrogen atmosphere.

Single Crystal X-ray Crystallography

Variable-temperature single-crystal X-ray diffraction data sets of **1** and **2** were collected with a Rigaku Saturn 924 diffractometer with Mo Kα radiation (λ=0.71073 Å) (220 K and 293 K for **1**, 200 K, 233 K and 293 K for **2**). The Crystal-clear software package was used to perform all data collections including empirical absorption corrections. The crystal structures of **1** and **2** were solved by direct methods and refined by the full-matrix method based on F^2 data by the SHELXL-97 software package. Non-hydrogen atoms were refined anisotropically by using reflections with $I > 2\sigma(I)$. Crystallographic data and structure refinements for **1** and **2** are listed in Table S1 and S5.

Dielectric Measurements

The powder-pressed pellets of compounds **1** and **2** coated with silver conducting glue on both sides were used in dielectric measurements. The temperature dependent

dielectric permittivity was measured on a Tonghui TH2828A over the frequency range from 50 kHz to 1 MHz, with an applied electric field of 1 V.

Ferroelastic Measurements

For ferroelastic properties, ferroelastic domain observations of compounds **1** and **2** were carried on an Olympus BX51TRF polarizing microscope in heating/cooling cycle. The temperature was controlled by the INSTEC HCC602 cooling/heating stage. Aqueous saturated solution (20 μL) of **1** was dropped on a prepared indium tin oxide (ITO)-coated glass, and thin film was obtained at heating stage of 353 K. The crystal **2** was directly observed under the polarizing microscope. According to a heating and cooling cycle, the transforming of domain structures of compounds **1** and **2** can be observed.

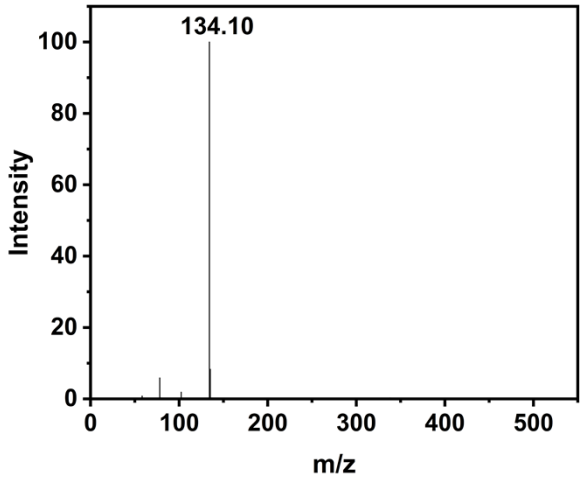

Figure S1. The mass spectrum of **[(**$CH_3)_3CN(CH_3)_2CH_2F]^+$.

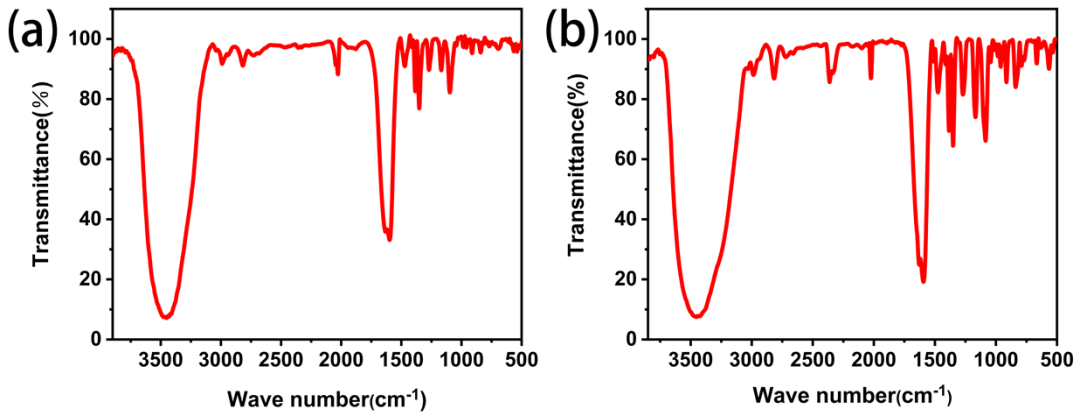

Figure S2. IR spectrums of **1** (a) and **2** (b) on a KBr-diluted pellet at room temperature.

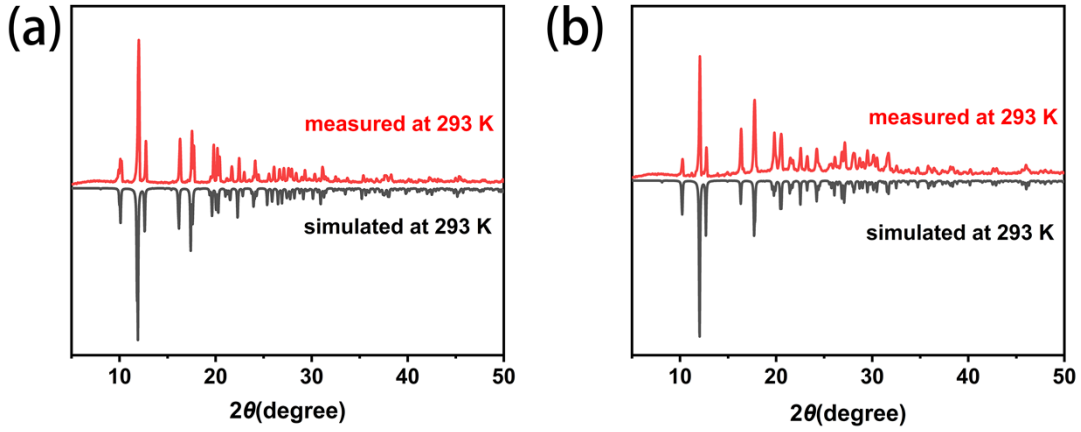

Figure S3. Powder XRD patterns of **1** (a) and **2** (b) at 293 K.

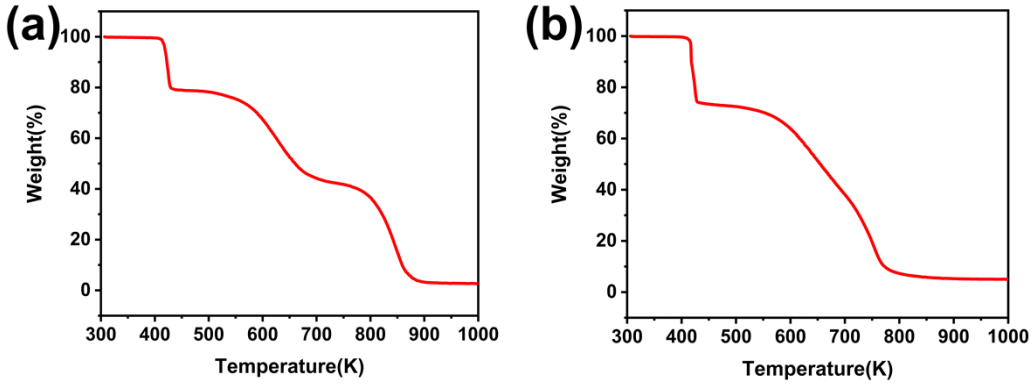

Figure S4. Thermogravimetric analysis curves of compounds **1**(a) and **2**(b).

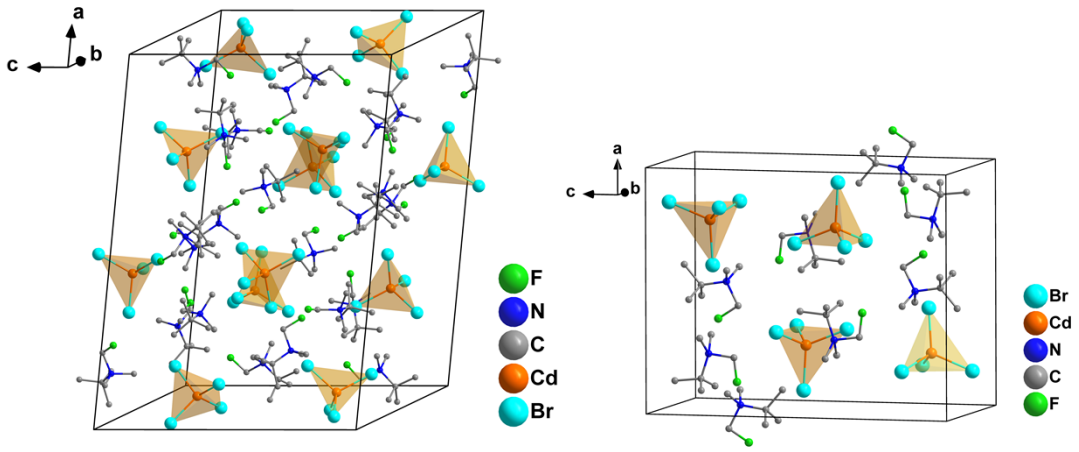

Figure S5. Structural packing diagrams of **1** at LTP_1 (left) and HTP_1 (right). All hydrogen atoms are omitted for clarity.

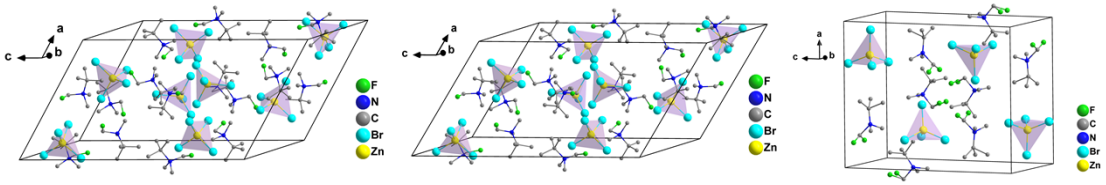

Figure S6. Structural packing diagrams of **2** at LTP_2 (left), ITP_2 (middle) and HTP_2 (right). All hydrogen atoms are omitted for clarity.

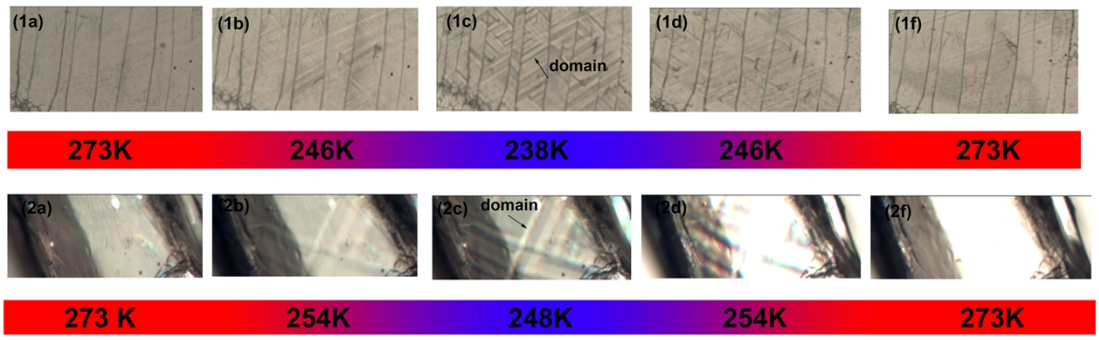

Figure S7. Evolution of the domain structures of compounds **1** and **2** during the heating and cooling process.

Table S1. Crystal data, data collection and structure refinement details of crystal **1** at 220 K and 293 K.

	220 K	293 K
Chemical Formula	$C_{14}H_{34}Br_4CdF_2N_2$	$C_{14}H_{34}Br_4CdF_2N_2$
Formula weight	700.47	700.47
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pnma*
a, Å	25.5761 (15)	14.014 (2)
b, Å	15.1486 (7)	10.0680
c, Å	18.9359 (11)	17.771 (3)
α, deg	90	90
β, deg	100.579 (6)	90
γ, deg	90	90
V, Å^3	7211.9 (7)	2507.3 (7)
Z	12	4
F(000)	4056	1352
μ, mm^{-1}	7.57	7.26
α, deg	90	90
	$-30 \le h \le 30$	$-16 \le h \le 15$
Index ranges	$-18 \le k \le 17$	$-11 \le k \le 11$
	$-22 \le l \le 22$	$-19 \le l \le 21$
D_{calcd}, g•cm^{-3}	1.935	1.856
Reflections measured	60486	10604
Reflections independent	12695	2338
Reflections used	7339	967
S	1.26	1.38
R_1	0.1314	0.0949
wR_2	0.3404	0.3067

Table S2. The key bond distances (Å) and angles (°) of **1** at 220 K and 293 K.

	F2—C16	1.419 (13)	C24—C27	1.536 (14)
	N5—C16	1.491 (14)	C24—C29	1.547 (15)
	N5—C15	1.502 (15)	F7—C5	1.390 (13)
	N5—C14	1.523 (14)	N1—C3	1.493 (14)
	N5—C10	1.526 (13)	N1—C5	1.505 (13)
	C10—C11	1.528 (14)	N1—C4	1.494 (13)
	C10—C13	1.515 (15)	N1—C6	1.533 (13)
	C10—C12	1.535 (14)	C6—C8	1.501 (14)
	F3—C22	1.425 (15)	C6—C7	1.505 (14)
	N3—C20	1.496 (15)	C6—C9	1.514 (13)
	N3—C22	1.499 (15)	F8—C45	1.423 (14)
	N3—C23	1.508 (13)	N6—C46	1.498 (14)
	N3—C21	1.506 (15)	N6—C45	1.496 (15)
220 K	C23—C47	1.522 (16)	N6—C49	1.498 (16)
	C23—C30	1.531 (15)	N6—C32	1.531 (13)
	C23—C48	1.536 (16)	C32—C33	1.527 (14)
	F5—C42	1.411 (15)	C32—C34	1.538 (15)
	N2—C41	1.493 (14)	C32—C35	1.534 (15)
	N2—C40	1.501 (15)	Cd1—Br4	2.585 (2)
	N2—C42	1.499 (14)	Cd1—Br3	2.593 (2)
	N2—C43	1.506 (14)	Cd1—Br1	2.596 (2)
	C37—C43	1.518 (14)	Cd1—Br2	2.600 (2)
	C38—C43	1.531 (15)	Cd3—Br7	2.576 (3)
	C39—C43	1.538 (14)	Cd3—Br8	2.589 (3)
	F6—C44	1.389 (15)	Cd3—Br5	2.589 (2)
	N4—C44	1.503 (14)	Cd3—Br6	2.598 (3)
	N4—C26	1.496 (14)	Cd2—Br12	2.588 (2)
	N4—C24	1.519 (13)	Cd2—Br11	2.590 (3)

	N4—C50	1.518 (13)	Cd2—Br10	2.596 (2)
	C24—C28	1.535 (14)	Cd2—Br9	2.595 (2)
	C16—N5—C15	109.7 (13)	N4—C24—C29	109.5 (10)
	C16—N5—C14	105.6 (12)	C28—C24—C29	107.3 (11)
	C15—N5—C14	105.9 (12)	C27—C24—C29	108.9 (12)
	C16—N5—C10	108.0 (9)	F6—C44—N4	107.9 (12)
	C15—N5—C10	111.1 (11)	C3—N1—C5	110.2 (11)
	C14—N5—C10	116.3 (10)	C3—N1—C4	109.2 (11)
	C11—C10—C13	112.1 (13)	C5—N1—C4	106.5 (11)
	C11—C10—N5	108.3 (11)	C3—N1—C6	113.9 (10)
	C13—C10—N5	111.5 (10)	C5—N1—C6	104.5 (8)
	C11—C10—C12	106.6 (13)	C4—N1—C6	112.3 (10)
220 K	C13—C10—C12	108.1 (12)	F7—C5—N1	105.5 (12)
	N5—C10—C12	110.1 (11)	C8—C6—C7	108.7 (11)
	F2—C16—N5	109.6 (12)	C8—C6—C9	107.6 (11)
	C20—N3—C22	114.7 (14)	C7—C6—C9	109.1 (11)
	C20—N3—C23	112.7 (12)	C8—C6—N1	107.8 (10)
	C22—N3—C23	107.6 (10)	C7—C6—N1	111.4 (11)
	C20—N3—C21	104.4 (13)	C9—C6—N1	112.1 (9)
	C22—N3—C21	106.7 (15)	C46—N6—C45	93.5 (13)
	C23—N3—C21	110.6 (13)	C46—N6—C49	123.2 (15)
	F3—C22—N3	107.1 (14)	C45—N6—C49	100.8 (13)
	C47—C23—N3	111.0 (13)	C46—N6—C32	112.3 (13)
	C47—C23—C30	102.7 (17)	C45—N6—C32	105.0 (10)
	N3—C23—C30	110.2 (12)	C49—N6—C32	116.2 (11)
	C47—C23—C48	116.1 (15)	C33—C32—N6	108.4 (10)
	N3—C23—C48	112.8 (12)	C33—C32—C34	110.3 (13)
	C30—C23—C48	103.0 (14)	N6—C32—C34	108.9 (11)

	C41—N2—C40	106.9 (13)	C33—C32—C35	107.6 (14)
	C41—N2—C42	106.5 (14)	N6—C32—C35	111.1 (11)
	C40—N2—C42	112.7 (14)	C34—C32—C35	110.5 (14)
	C41—N2—C43	113.0 (12)	F8—C45—N6	113.2 (13)
	C40—N2—C43	112.2 (12)	Br4—Cd1—Br3	104.32 (7)
	C42—N2—C43	105.6 (10)	Br4—Cd1—Br1	110.34 (7)
	F5—C42—N2	101.6 (12)	Br3—Cd1—Br1	116.51 (7)
	N2—C43—C37	108.1 (11)	Br4—Cd1—Br2	113.31 (8)
	N2—C43—C39	111.5 (12)	Br3—Cd1—Br2	106.63 (7)
	C37—C43—C39	114.0 (13)	Br1—Cd1—Br2	105.91 (7)
220 K	N2—C43—C38	109.7 (13)	Br7—Cd3—Br8	113.35 (9)
	C37—C43—C38	110.8 (14)	Br7—Cd3—Br5	108.63 (9)
	C39—C43—C38	102.5 (15)	Br8—Cd3—Br5	103.73 (8)
	C44—N4—C26	106.8 (11)	Br7—Cd3—Br6	108.75(10)
	C44—N4—C24	107.1 (9)	Br8—Cd3—Br6	112.12 (9)
	C26—N4—C24	114.4 (10)	Br5—Cd3—Br6	110.12 (8)
	C44—N4—C50	109.1 (11)	Br12—Cd2—Br11	108.70 (8)
	C26—N4—C50	108.5 (11)	Br12—Cd2—Br10	109.28 (8)
	C24—N4—C50	110.8 (10)	Br11—Cd2—Br10	113.05 (9)
	N4—C24—C28	110.5 (10)	Br12—Cd2—Br9	111.93 (9)
	N4—C24—C27	111.5 (10)	Br11—Cd2—Br9	105.38 (9)
	C28—C24—C27	109.0 (11)	Br10—Cd2—Br9	108.50 (8)
	Br1—Cd1	2.5633 (8)	C2—C12	1.552 (8)
	Cd1—Br1^{i}	2.5633 (8)	C6—N2	1.516 (6)
	Cd1—Br3	2.5785 (10)	C6—C7	1.531 (6)
293 K	Cd1—Br2	2.5994 (10)	C6—C7^{i}	1.531 (6)
	N1—C2	1.500 (8)	C6—C13	1.518 (9)
	N1—C11	1.511 (8)	N2—C9	1.525 (7)
	N1—C4	1.536 (7)	N2—C10	1.540 (6)

	N1—C4^{i}	1.536 (7)	N2—C10^{i}	1.540 (6)
	C2—C3^{i}	1.559 (6)	F1—C9	1.398 (8)
	C2—C3	1.559 (6)	F2—C11	1.392 (8)
	Br1—Cd1—Br1^{i}	110.61 (4)	C3^{i}—C2—C12	103.5 (4)
	Br1—Cd1—Br3	108.77 (2)	C3—C2—C12	103.5 (4)
	Br1^{i}—Cd1—Br3	108.77 (2)	N2—C6—C7	107.3 (3)
	Br1—Cd1—Br2	106.89 (2)	N2—C6—C7^{i}	107.3 (3)
	Br1^{i}—Cd1—Br2	106.89 (2)	C7—C6—C7^{i}	117.1 (6)
293 K	Br3—Cd1—Br2	114.88 (4)	N2—C6—C13	122.2 (5)
	C2—N1—C11	100.0 (4)	C7—C6—C13	101.8 (4)
	C2—N1—C4	124.6 (4)	C7^{i}—C6—C13	101.8 (4)
	C11—N1—C4	102.2 (5)	C6—N2—C9	107.9 (4)
	C2—N1—C4^{i}	124.6 (4)	C6—N2—C10	109.0 (3)
	C11—N1—C4^{i}	102.2 (5)	C9—N2—C10	108.4 (3)
	C4—N1—C4^{i}	99.0 (6)	C6—N2—C10^{i}	109.0 (3)
	N1—C2—C3^{i}	103.8 (4)	C9—N2—C10^{i}	108.4 (3)
	N1—C2—C3	103.8 (4)	C10—N2—C10^{i}	114.0 (6)
	C3^{i}—C2—C3	128.7 (7)	F1—C9—N2	96.3 (5)
	N1—C2—C12	113.9 (7)	F2—C11—N1	104.7 (5)

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Table S3. Hydrogen bonds at 220 K for **1**.

D——H···A	D——H	H···A	D···A	<DHA
C49—H49*C*···Br5^{i}	0.96	2.91	3.82 (2)	160
C46—H46*B*···F8	0.96	2.14	2.69 (3)	115
C45—H45*A*···Br11	0.97	2.97	3.78 (2)	142
C35—H35*C*···Br9^{ii}	0.96	3.08	4.029 (19)	168
C34—H34*A*···Br5^{i}	0.96	3.04	3.98 (2)	166
C8—H8*A*···F5	0.96	2.57	3.20 (2)	123
C5—H5*A*···Br1^{ii}	0.97	3.08	3.636 (14)	118
C4—H4*B*···Br10	0.96	3.21	4.061 (16)	149
C3—H3*B*···Br10	0.96	3.10	3.885 (17)	140
C3—H3*A*···F8	0.96	2.45	3.33 (2)	152
C50—H50*C*···Br2^{iii}	0.96	3.03	3.907 (18)	153
C50—H50*B*···Br12	0.96	3.17	3.926 (17)	137
C44—H44*B*···Br2^{iii}	0.97	3.06	3.811 (17)	135
C44—H44*A*···Br12^{iv}	0.97	2.97	3.563 (14)	121
C29—H29*C*···Br3^{iv}	0.96	3.08	3.940 (19)	150
C29—H29*C*···F8	0.96	2.56	3.30 (2)	134
C29—H29*B*···F7	0.96	2.58	3.26 (2)	128
C28—H28*C*···Br1^{iv}	0.96	2.90	3.792 (17)	155
C28—H28*A*···Br2^{iii}	0.96	3.08	4.033 (19)	173
C27—H27*A*···Br3^{ii}	0.96	3.12	4.063 (16)	166
C42—H42*A*···Br4^{v}	0.97	2.99	3.87 (2)	151
C41—H41*C*···Br9^{ii}	0.96	3.07	3.823 (18)	137
C41—H41*B*···Br7^{vi}	0.96	2.92	3.86 (2)	165
C41—H41*A*···F3	0.96	2.49	3.08 (2)	119
C40—H40*A*···Br5	0.96	2.95	3.62 (2)	128
C39—H39*C*···Br7^{vi}	0.96	3.11	3.95 (2)	147
C39—H39*B*···Br7^{vii}	0.96	3.08	3.991 (19)	158

C48—H48*A*···Br8^{vi}	0.96	3.12	4.03 (2)	159
C30—H30*C*···Br6	0.96	3.04	3.98 (2)	165
C30—H30*B*···Br6^{viii}	0.96	3.09	4.00 (2)	158
C21—H21*C*···F3	0.96	2.20	2.69 (3)	110
C21—H21*A*···Br9	0.96	3.05	3.99 (2)	168
C20—H20*C*···Br10	0.96	3.00	3.848 (17)	147
C20—H20*B*···Br9	0.96	3.05	3.90 (2)	149
C20—H20*A*···Br6	0.96	3.01	3.900 (19)	156
C16—H16*B*···Br1^{v}	0.97	3.01	3.86 (2)	147
C16—H16*A*···Br5	0.97	2.97	3.87 (2)	155
C14—H14*B*···Br6	0.96	3.15	3.872 (17)	133
C14—H14*B*···Br5	0.96	3.06	3.85 (2)	140
C11—H11*C*···Br3^{ix}	0.96	3.15	4.04 (2)	155

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*+2; (iv) −*x*+1, *y*−1/2, −*z*+3/2; (v) −*x*+1, *y*+1/2, −*z*+3/2; (vi) −*x*+2, *y*−1/2, −*z*+3/2; (vii) *x*, −*y*+3/2, *z*−1/2; (viii) −*x*+2, −*y*+1, −*z*+2; (ix) −*x*+1, −*y*+1, −*z*+2.

Table S4. Hydrogen bonds at 293 K for **1**.

D——H···A	D——H	H···A	D···A	<DHA
C12—H12*C*···Br1^{ii}	0.96	3.07	4.004 (6)	164
C12—H12*B*···Br1^{iii}	0.96	3.07	4.004 (6)	164
C12—H12*A*···Br2	0.96	2.92	3.866 (15)	168
C13—H13*A*···Br3^{iv}	0.96	3.01	3.948 (8)	165
C9—H9*B*···Br1^{v}	0.97	2.80	3.684 (3)	152
C9—H9*A*···Br1^{vi}	0.97	2.80	3.684 (3)	152
C7—H7*C*···F1	0.96	1.64	2.215 (9)	114
C10—H10*C*···Br1^{ii}	0.96	3.06	3.920 (6)	151
C3—H3*C*···F2	0.96	1.71	2.239 (9)	111
C3—H3*A*···Br1	0.96	3.10	3.829 (8)	134
C3—H3*A*···Br1	0.96	3.10	3.829 (8)	134
C3—H3*C*···F2	0.96	1.71	2.239 (9)	111
C10—H10*C*···Br1^{ii}	0.96	3.06	3.920 (6)	151
C7—H7*C*···F1	0.96	1.64	2.215 (9)	114
C9—H9*A*···Br1^{vi}	0.97	2.80	3.684 (3)	152
C9—H9*B*···Br1^{v}	0.97	2.80	3.684 (3)	152
C13—H13*A*···Br3^{iv}	0.96	3.01	3.948 (8)	165
C12—H12*A*···Br2	0.96	2.92	3.866 (15)	168
C12—H12*B*···Br1^{iii}	0.96	3.07	4.004 (6)	164
C12—H12*C*···Br1^{ii}	0.96	3.07	4.004 (6)	164

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, *y*+1/2, −*z*+1; (iv) *x*−1, *y*, *z*; (v) −*x*+1/2, *y*+1/2, *z*+1/2; (vi) −*x*+1/2, −*y*, *z*+1/2.

Table S5. Crystal data, data collection and structure refinement details of crystal **2** at 200 K, 233 K and 293 K.

	200 K	233 K	293 K
Chemical Formula	$2(C_7H_{17}FN)\cdot Br_4Zn$	$2(C_7H_{17}FN)\cdot Br_4Zn$	$2(C_7H_{16}FN)\cdot Br_4Zn$
Formula weight	653.44	653.44	651.41
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	*Pnma*
a, Å	14.1602 (4)	14.101 (3)	13.9404 (10)
b, Å	15.8563 (4)	15.970 (2)	9.9595 (6)
c, Å	24.3724 (8)	25.108 (4)	17.3700 (12)
α, deg	90	90	90
β, deg	122.111 (2)	124.168 (9)	90
γ, deg	90	90	90
V, Å^3	4635.1 (2)	4678.2 (14)	2411.6 (3)
Z	8	8	4
F(000)	2560	2560	1272
μ, mm^{-1}	7.97	7.90	7.66
Radiation (Mo Kα)	0.71073	0.71073	0.71073
Index ranges	$-13 \le h \le 16$ $-18 \le k \le 18$ $-28 \le l \le 28$	$-14 \le h \le 16$ $-18 \le k \le 18$ $-29 \le l \le 20$	$-16 \le h \le 16$ $-11 \le k \le 11$ $-18 \le l \le 20$
D_{calcd}, g•cm^{-3}	1.873	1.856	1.794
Reflections measured	36975	21005	16463
Reflections independent	8154	7199	2256
Reflections used	6435	3770	1140
S	1.20	1.27	2.07
R_1	0.0688	0.1284	0.1142

wR_2	0.1798	0.3249	0.3479

Table S6. The key bond distances (Å) and angles (°) of **2** at 200 K, 233 K and 293 K.

	F1—C7	1.379 (11)	N3—C15	1.554 (10)
	N1—C7	1.509 (11)	C15—C18	1.500 (17)
	N1—C6	1.510 (10)	C15—C16	1.515 (17)
	N1—C5	1.516 (10)	C15—C17	1.521 (13)
	N1—C1	1.579 (11)	F4—C28	1.377 (9)
	C1—C2	1.504 (12)	N4—C26	1.502 (11)
	C1—C4	1.529 (14)	N4—C28	1.504 (11)
	C1—C3	1.535 (12)	N4—C27	1.517 (10)
	F2—C14	1.363 (11)	N4—C22	1.593 (9)
200 K	N2—C14	1.512 (11)	C22—C25	1.501 (13)
	N2—C12	1.516 (13)	C22—C23	1.508 (11)
	N2—C13	1.531 (12)	C22—C24	1.535 (13)
	N2—C8	1.573 (9)	Br1—Zn1	2.4127 (13)
	C8—C10	1.515 (12)	Br2—Zn1	2.4162 (11)
	C8—C9	1.522 (13)	Br3—Zn1	2.4146 (13)
	C8—C11	1.537 (13)	Br4—Zn1	2.4346 (13)
	F3—C20	1.306 (16)	Br5—Zn2	2.4312 (12)
	N3—C21	1.491 (12)	Br6—Zn2	2.4034 (15)
	N3—C19	1.505 (15)	Br7—Zn2	2.4219 (12)
	N3—C20	1.512 (14)	Br8—Zn2	2.4014 (12)
	C7—N1—C6	103.4 (7)	C18—C15—C16	111.5 (11)
	C7—N1—C5	107.9 (7)	C18—C15—C17	108.7 (10)
	C6—N1—C5	107.1 (6)	C16—C15—C17	107.2 (8)
	C7—N1—C1	112.5 (6)	C18—C15—N3	107.6 (8)
	C6—N1—C1	111.4 (6)	C16—C15—N3	111.3 (9)
	C5—N1—C1	113.8 (7)	C17—C15—N3	110.4 (7)
	C2—C1—C4	109.4 (8)	F3—C20—N3	108.8 (11)
	C2—C1—C3	107.9 (7)	C26—N4—C28	110.5 (6)

	C4—C1—C3	109.8 (8)	C26—N4—C27	108.3 (7)
	C2—C1—N1	110.6 (7)	C28—N4—C27	107.2 (7)
	C4—C1—N1	109.5 (6)	C26—N4—C22	111.5 (6)
	C3—C1—N1	109.6 (7)	C28—N4—C22	108.1 (6)
	F1—C7—N1	108.3 (7)	C27—N4—C22	111.1 (6)
200 K	C14—N2—C12	107.2 (7)	C25—C22—C23	111.6 (7)
	C14—N2—C13	103.6 (7)	C25—C22—C24	109.4 (8)
	C12—N2—C13	107.5 (8)	C23—C22—C24	108.6 (7)
	C14—N2—C8	113.9 (6)	C25—C22—N4	110.1 (6)
	C12—N2—C8	111.8 (7)	C23—C22—N4	109.7 (6)
	C13—N2—C8	112.3 (6)	C24—C22—N4	107.4 (6)
	C10—C8—C9	108.8 (8)	F4—C28—N4	107.1 (7)
	C10—C8—C11	111.0 (8)	Br1—Zn1—Br3	112.63 (5)
	C9—C8—C11	108.9 (7)	Br1—Zn1—Br2	108.06 (4)
	C10—C8—N2	110.3 (6)	Br3—Zn1—Br2	105.80 (5)
	C9—C8—N2	108.7 (7)	Br1—Zn1—Br4	109.33 (5)
	C11—C8—N2	109.1 (7)	Br3—Zn1—Br4	107.39 (4)
	F2—C14—N2	107.3 (8)	Br2—Zn1—Br4	113.69 (5)
	C21—N3—C19	108.1 (7)	Br8—Zn2—Br6	115.65 (5)
	C21—N3—C20	110.2 (8)	Br8—Zn2—Br7	109.00 (5)
	C19—N3—C20	99.4 (9)	Br6—Zn2—Br7	107.88 (5)
	C21—N3—C15	114.2 (7)	Br8—Zn2—Br5	105.48 (4)
200 K	C19—N3—C15	111.2 (8)	Br6—Zn2—Br5	109.57 (5)
	C20—N3—C15	112.5 (7)	Br7—Zn2—Br5	109.13 (5)
	F1—C7	1.326 (7)	N3—C20	1.550 (8)
	N1—C5	1.493 (7)	C15—C17	1.525 (7)
	N1—C7	1.489 (8)	C15—C16	1.550 (9)
	N1—C6	1.494 (7)	C15—C18	1.558 (9)
	N1—C1	1.509 (7)	N4—C26	1.508 (9)

	C1—C3	1.520 (8)	N4—C27	1.514 (8)
	C1—C4	1.529 (7)	N4—C22	1.524 (5)
	C1—C2	1.527 (6)	N4—C28	1.537 (9)
	F2—C14	1.407 (9)	C22—C24	1.537 (10)
	N2—C8	1.502 (5)	C22—C25	1.516 (8)
	N2—C14	1.505 (8)	C22—C23	1.562 (9)
233 K	N2—C12	1.508 (8)	Br1—Zn1	2.434 (2)
	N2—C13	1.520 (9)	Br2—Zn1	2.3983 (13)
	C8—C9	1.529 (9)	Br3—Zn1	2.3935 (12)
	C8—C11	1.538 (7)	Br4—Zn1	2.4015 (14)
	C8—C10	1.541 (9)	Br5—Zn2	2.3867 (12)
	F3—C21	1.337 (7)	Br6—Zn2	2.3995 (12)
	N3—C15	1.501 (5)	Br7—Zn2	2.4144 (16)
	N3—C19	1.496 (8)	Br8—Zn2	2.4392 (16)
	N3—C21	1.528 (9)	F4—C28	1.472 (10)
	C5—N1—C7	108.1 (6)	N3—C15—C17	110.3 (4)
	C5—N1—C6	104.4 (5)	N3—C15—C16	107.7 (4)
	C7—N1—C6	115.6 (5)	C17—C15—C16	102.7 (5)
	C5—N1—C1	110.5 (6)	N3—C15—C18	105.9 (4)
	C7—N1—C1	109.2 (4)	C17—C15—C18	109.7 (5)
	C6—N1—C1	108.9 (5)	C16—C15—C18	120.4 (5)
	N1—C1—C3	112.7 (4)	F3—C21—N3	106.9 (7)
	N1—C1—C4	111.1 (6)	C26—N4—C27	104.4 (5)
	C3—C1—C4	106.6 (7)	C26—N4—C22	107.2 (5)
	N1—C1—C2	108.7 (5)	C27—N4—C22	115.7 (5)
	C3—C1—C2	114.8 (5)	C26—N4—C28	115.2 (5)
	C4—C1—C2	102.5 (4)	C27—N4—C28	104.6 (6)
	F1—C7—N1	111.9 (6)	C22—N4—C28	109.9 (4)

	C8—N2—C14	114.2 (4)	C24—C22—C25	104.1 (6)
	C8—N2—C12	113.0 (4)	C24—C22—N4	106.0 (5)
	C14—N2—C12	104.0 (6)	C25—C22—N4	113.7 (5)
233 K	C8—N2—C13	107.8 (5)	C24—C22—C23	113.0 (6)
	C14—N2—C13	106.9 (5)	C25—C22—C23	99.7 (6)
	C12—N2—C13	110.8 (6)	N4—C22—C23	119.5 (5)
	N2—C8—C9	110.2 (5)	Br3—Zn1—Br2	106.04 (5)
	N2—C8—C11	114.8 (4)	Br3—Zn1—Br4	108.68 (6)
	C9—C8—C11	113.0 (6)	Br2—Zn1—Br4	107.00 (6)
	N2—C8—C10	107.8 (5)	Br3—Zn1—Br1	110.54 (6)
	C9—C8—C10	106.4 (6)	Br2—Zn1—Br1	114.17 (6)
	C11—C8—C10	104.2 (6)	Br4—Zn1—Br1	110.18 (6)
	F2—C14—N2	108.6 (7)	Br5—Zn2—Br6	108.20 (4)
	C15—N3—C19	110.7 (5)	Br5—Zn2—Br7	105.77 (6)
	C15—N3—C21	108.6 (4)	Br6—Zn2—Br7	112.63 (5)
	C19—N3—C21	105.2 (6)	Br5—Zn2—Br8	112.58 (5)
	C15—N3—C20	101.8 (4)	Br6—Zn2—Br8	108.52 (6)
	C19—N3—C20	109.1 (6)	Br7—Zn2—Br8	109.18 (4)
	C21—N3—C20	121.3 (5)	F4—C28—N4	94.5 (6)
293 K	F1—C18	1.410 (8)	N1—C6^{ii}	1.560 (7)
	C10—C12	1.510 (11)	N1—C6	1.560 (7)
	C10—N2	1.527 (6)	C2—C3	1.533 (9)
	C10—C11	1.651 (8)	C2—C3^{ii}	1.533 (9)
	C10—C11^{i}	1.651 (8)	C2—C5	1.579 (10)
	C16—N2	1.5317 (13)	C8—F3^{ii}	1.431 (8)
	N2—C18	1.5305 (13)	C8—F3	1.431 (8)
	N2—C16^{i}	1.5316 (13)	Zn1—Br3^{ii}	2.3850 (9)
	C18—F1^{i}	1.410 (8)	Br1—Zn1	2.4052 (13)
	N1—C2	1.526 (8)	Br2—Zn1	2.4150 (12)

	N1—C8	1.541 (10)	Br3—Zn1	2.3851 (9)
293 K				
	C18—F1—F1^{i}	51.8 (4)	C2—N1—C6	111.6 (4)
	C12—C10—N2	117.0 (7)	C8—N1—C6	90.2 (4)
	C12—C10—C11	95.5 (5)	C6^{ii}—N1—C6	122.0 (7)
	N2—C10—C11	115.8 (4)	N1—C2—C3	124.8 (4)
	C12—C10—C11^{i}	95.5 (5)	N1—C2—C3^{ii}	124.8 (4)
	N2—C10—C11^{i}	115.8 (4)	C3—C2—C3^{ii}	109.0 (8)
	C11—C10—C11^{i}	113.8 (8)	N1—C2—C5	106.5 (6)
	C10—N2—C18	106.0 (3)	C3—C2—C5	86.6 (6)
	C10—N2—C16^{i}	120.82 (17)	C3^{ii}—C2—C5	86.6 (6)
	C18—N2—C16^{i}	103.66 (13)	F3^{ii}—C8—F3	135.3 (12)
	C10—N2—C16	120.82 (17)	F3^{ii}—C8—N1	109.2 (6)
	C18—N2—C16	103.66 (13)	F3—C8—N1	109.2 (6)
	C16^{i}—N2—C16	99.58 (13)	Br3^{ii}—Zn1—Br3	110.87 (5)
	F1—C18—F1^{i}	76.4 (8)	Br3^{ii}—Zn1—Br1	108.23 (4)
	F1—C18—N2	108.2 (6)	Br3—Zn1—Br1	108.23 (4)
	F1^{i}—C18—N2	108.2 (6)	Br3^{ii}—Zn1—Br2	108.00 (3)
	Br1—Zn1—Br2	113.54 (5)	Br3—Zn1—Br2	108.00 (3)

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

Figure S7. Hydrogen bonds at 200 K for **2**.

D——H···A	D——H	H···A	D···A	<DHA
C28—H28*B*···Br3^{i}	0.97	3.01	3.733 (9)	133
C28—H28*B*···Br1^{i}	0.97	3.00	3.784 (9)	138
C28—H28*A*···Br4	0.97	3.10	4.050 (9)	165
C27—H27*C*···Br8^{ii}	0.96	3.07	3.642 (10)	120
C27—H27*A*···Br7^{iii}	0.96	3.12	3.939 (9)	144
C26—H26*C*···Br7^{iii}	0.96	2.93	3.852 (7)	163
C26—H26*B*···Br3^{i}	0.96	3.01	3.862 (9)	148
C24—H24*C*···Br5^{iv}	0.96	2.87	3.797 (8)	163
C24—H24*B*···Br8^{ii}	0.96	3.10	4.049 (9)	172
C21—H21*A*···Br7^{v}	0.96	3.02	3.971 (12)	172
C20—H20*A*···Br5	0.97	2.76	3.668 (12)	156
C19—H19*C*···Br4^{vi}	0.96	3.08	3.790 (10)	132
C19—H19*B*···Br6	0.96	3.05	3.909 (12)	150
C19—H19*A*···Br2^{vi}	0.96	2.85	3.740 (14)	154
C17—H17*A*···Br5	0.96	2.98	3.915 (11)	166
C16—H16*A*···Br7^{v}	0.96	3.01	3.967 (12)	172
C14—H14*B*···Br7	0.97	2.98	3.809 (9)	144
C14—H14*A*···Br3	0.97	3.01	3.857 (8)	147
C13—H13*C*···Br3	0.96	3.03	3.886 (9)	150
C13—H13*B*···Br6^{v}	0.96	2.99	3.894 (9)	157
C13—H13*A*···F3	0.96	2.60	3.511 (17)	159
C12—H12*A*···Br4	0.96	3.09	3.758 (9)	128
C12—H12*A*···Br3	0.96	3.10	3.896 (10)	141
C11—H11*C*···Br6^{v}	0.96	3.13	4.088 (10)	173
C10—H10*B*···Br1^{i}	0.96	3.12	3.964 (9)	147
C9—H9*B*···Br8^{v}	0.96	2.96	3.689 (10)	133
C9—H9*A*···Br2^{vii}	0.96	3.03	3.951 (9)	162

C7—H7*B*···Br8	0.97	2.93	3.823 (8)	154
C7—H7*A*···Br5^{viii}	0.97	3.00	3.956 (9)	167
C6—H6*C*···Br5^{viii}	0.96	3.02	3.954 (10)	166
C5—H5*B*···Br1^{ix}	0.96	2.99	3.867 (10)	152
C2—H2*B*···Br2^{viii}	0.96	3.09	3.902 (10)	143
C2—H2*B*···Br2^{viii}	0.96	3.09	3.902 (10)	143
C5—H5*B*···Br1^{ix}	0.96	2.99	3.867 (10)	152
C6—H6*C*···Br5^{viii}	0.96	3.02	3.954 (10)	166
C7—H7*A*···Br5^{viii}	0.97	3.00	3.956 (9)	167
C7—H7*B*···Br8	0.97	2.93	3.823 (8)	154
C9—H9*A*···Br2^{vii}	0.96	3.03	3.951 (9)	162
C9—H9*B*···Br8^{v}	0.96	2.96	3.689 (10)	133
C10—H10*B*···Br1^{i}	0.96	3.12	3.964 (9)	147
C11—H11*C*···Br6^{v}	0.96	3.13	4.088 (10)	173
C12—H12*A*···Br3	0.96	3.10	3.896 (10)	141
C12—H12*A*···Br4	0.96	3.09	3.758 (9)	128
C13—H13*A*···F3	0.96	2.60	3.511 (17)	159
C13—H13*B*···Br6^{v}	0.96	2.99	3.894 (9)	157
C13—H13*C*···Br3	0.96	3.03	3.886 (9)	150
C14—H14*A*···Br3	0.97	3.01	3.857 (8)	147
C14—H14*B*···Br7	0.97	2.98	3.809 (9)	144
C16—H16*A*···Br7^{v}	0.96	3.01	3.967 (12)	172
C17—H17*A*···Br5	0.96	2.98	3.915 (11)	166
C19—H19*A*···Br2^{vi}	0.96	2.85	3.740 (14)	154
C19—H19*B*···Br6	0.96	3.05	3.909 (12)	150
C19—H19*C*···Br4^{vi}	0.96	3.08	3.790 (10)	132
C20—H20*A*···Br5	0.97	2.76	3.668 (12)	156
C21—H21*A*···Br7^{v}	0.96	3.02	3.971 (12)	172
C24—H24*B*···Br8^{ii}	0.96	3.10	4.049 (9)	172

C24—H24*C*···Br5^{iv}	0.96	2.87	3.797 (8)	163
C26—H26*B*···Br3^{i}	0.96	3.01	3.862 (9)	148
C26—H26*C*···Br7^{iii}	0.96	2.93	3.852 (7)	163
C27—H27*A*···Br7^{iii}	0.96	3.12	3.939 (9)	144
C27—H27*C*···Br8^{ii}	0.96	3.07	3.642 (10)	120
C28—H28*A*···Br4	0.97	3.10	4.050 (9)	165
C28—H28*B*···Br1^{i}	0.97	3.00	3.784 (9)	138
C28—H28*B*···Br3^{i}	0.97	3.01	3.733 (9)	133

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) *x*−1, *y*, *z*; (iv) *x*, −*y*+3/2, *z*+1/2; (v) −*x*+2, *y*+1/2, −*z*+3/2; (vi) *x*+1, *y*, *z*; (vii) *x*+1, −*y*+3/2, *z*+1/2; (viii) −*x*+1, −*y*+1, −*z*+1; (ix) *x*, −*y*+3/2, *z*−1/2.

Figure S8. Hydrogen bonds at 233 K for **2**.

D——H···A	D——H	H···A	D···A	<DHA
C20—H20*B*···Br4^{i}	0.96	3.04	3.851 (4)	143
C25—H25*C*···F4	0.96	2.52	3.001 (17)	111
C24—H24*A*···F4	0.96	1.38	2.185 (15)	137
C21—H21*B*···Br7^{ii}	0.97	3.19	3.804 (6)	123
C21—H21*B*···Br6^{ii}	0.97	2.96	3.828 (7)	150
C19—H19*B*···Br4^{i}	0.96	3.21	3.885 (7)	129
C17—H17*B*···Br7^{iii}	0.96	3.10	4.017 (9)	160
C16—H16*B*···Br3^{iii}	0.96	2.83	3.766 (5)	166
C14—H14*A*···Br7	0.97	2.95	3.822 (6)	150
C13—H13*B*···Br8	0.96	3.17	3.655 (5)	113
C12—H12*A*···Br1^{iv}	0.96	2.95	3.829 (7)	153
C11—H11*B*···Br5^{v}	0.96	3.01	3.906 (7)	156
C7—H7*A*···Br2^{vi}	0.97	2.88	3.714 (4)	145
C6—H6*C*···Br6^{ii}	0.96	3.11	3.951 (8)	147
C6—H6*A*···F2	0.96	2.64	3.377 (9)	134
C5—H5*A*···F2	0.96	2.31	3.265 (9)	172
C4—H4*B*···Br1^{vi}	0.96	3.06	3.858 (7)	141
C4—H4*A*···F1	0.96	1.95	2.739 (16)	139
C2—H2*C*···Br1^{vi}	0.96	3.15	4.109 (5)	174

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) −*x*, *y*+1/2, −*z*+3/2; (v) *x*−1, −*y*+1/2, *z*−1/2; (vi) −*x*+1, −*y*, −*z*+2.

Figure S9. Hydrogen bonds at 293 K for **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*B*···Br2^{iii}	0.96	3.26	3.905 (2)	126
C12—H12*C*···Br3^{iv}	0.96	2.88	3.823 (8)	168
C12—H12*B*···Br3^{v}	0.96	2.88	3.823 (8)	168
C12—H12*A*···Br2^{vi}	0.96	2.92	3.834 (13)	160
C11—H11*B*···Br2^{vi}	0.96	2.92	3.797 (11)	153
C11—H11*A*···F1	0.96	1.92	2.493 (19)	116
C11—H11*A*···F1	0.96	1.92	2.493 (19)	116
C11—H11*B*···Br2^{vi}	0.96	2.92	3.797 (11)	153
C12—H12*A*···Br2^{vi}	0.96	2.92	3.834 (13)	160
C12—H12*B*···Br3^{v}	0.96	2.88	3.823 (8)	168
C12—H12*C*···Br3^{iv}	0.96	2.88	3.823 (8)	168

Symmetry codes: (iii) −*x*+3/2, −*y*+1, *z*+1/2; (iv) *x*+1/2, *y*, −*z*+1/2; (v) *x*+1/2, −*y*+1/2, −*z*+1/2; (vi) −*x*+1, −*y*+1, −*z*.