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Supporting Information

Modulating molecular structures and dielectric transitions in organic-inorganic hybrid crystals†

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Table S6 Hydrogen-Bond Geometry (Å, deg) for the weak N–H···Br interactions at 343 K and 253 K in **3**.

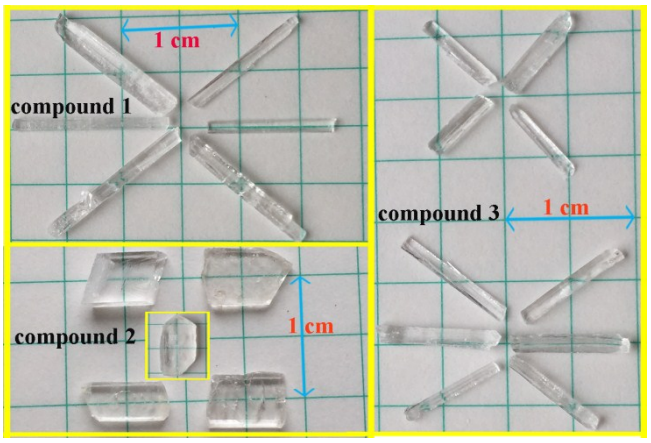

Figure S1. Colorless crystals of compound **1**, **2** and **3**

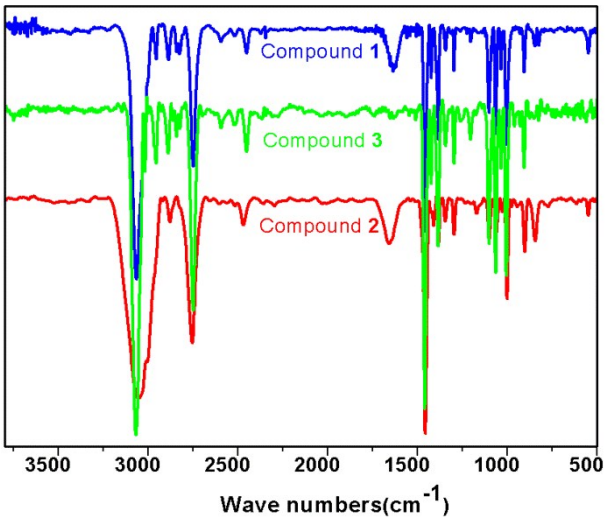

Figure S2. Infrared (IR) spectra of solid **1**, **2** and **3** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.

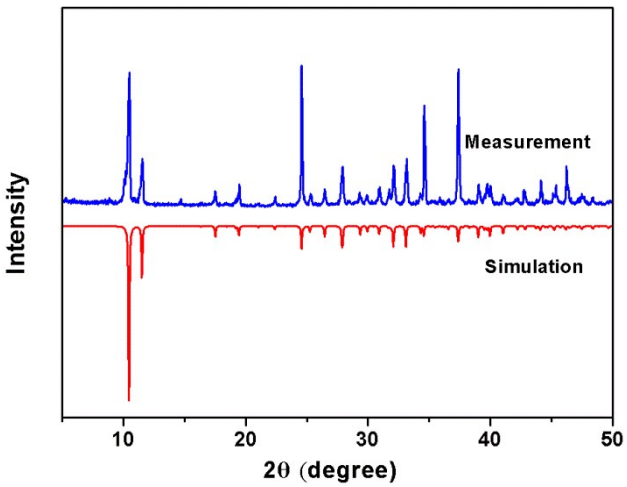

Figure S3. Experimental powder diffraction (PXRD) pattern of compound **1** matches very well with the simulated pattern in terms of the crystal structures at room temperature.

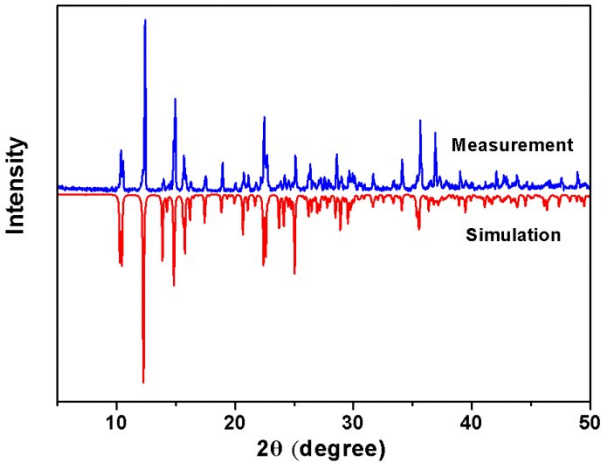

Figure S4. Experimental powder diffraction (PXRD) pattern of compound **2** matches very well with the simulated pattern in terms of the crystal structures at room temperature.

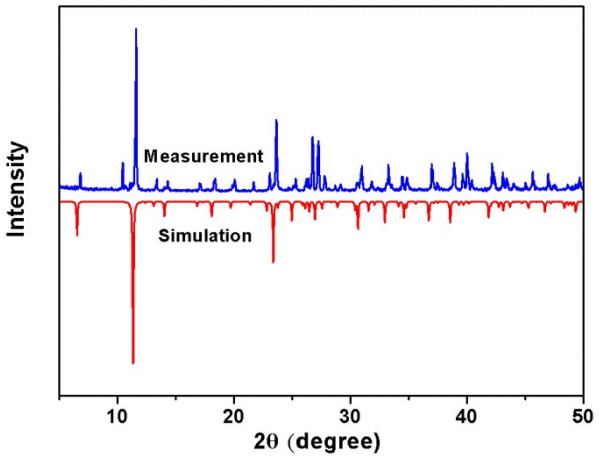

Figure S5. Experimental powder diffraction (PXRD) pattern of compound **3** matches very well with the simulated pattern in terms of the crystal structures at room temperature.

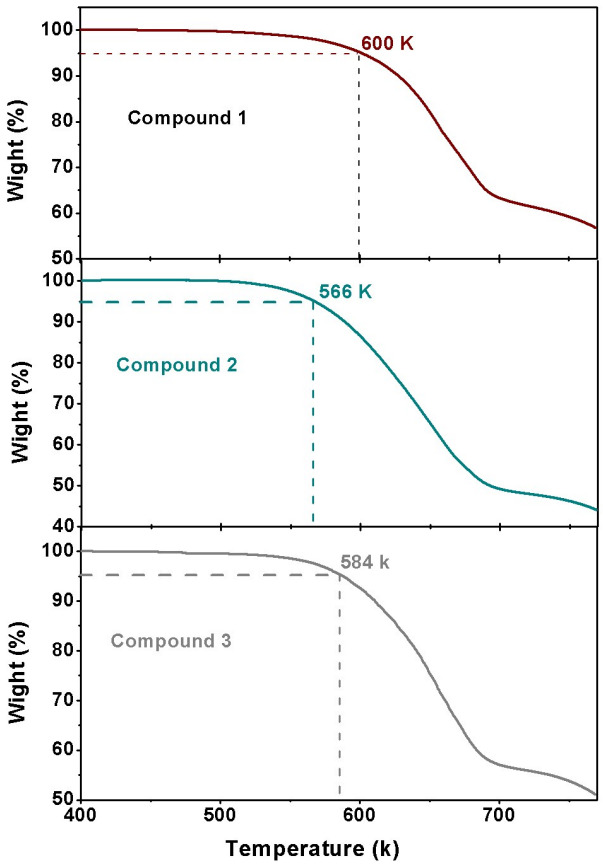

Figure S6. TGA measurements of **1**, **2** and **3** in the temperature range of 400−770 K.

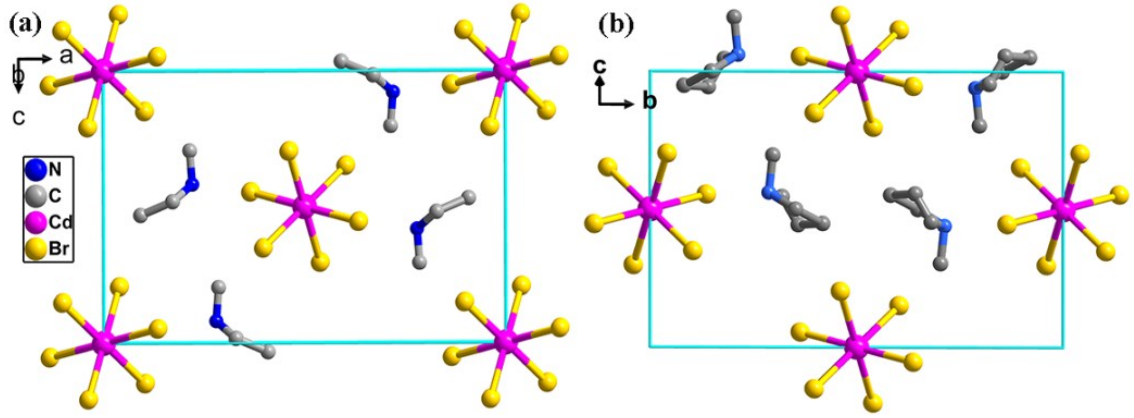

Figure S7. The packing diagram structures of **1** at 263 (a) and 293 (b) K. The hydrogen atoms are omitted for clarity.

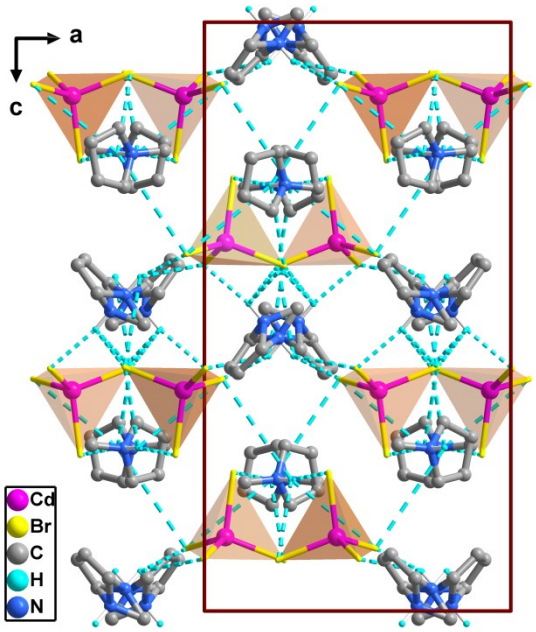

Figure S8. The packing diagram structure of **2** at 293 K. The dashed lines denote the N-H···Br interactions. The hydrogen atoms of C atoms are omitted for clarity.

(a)

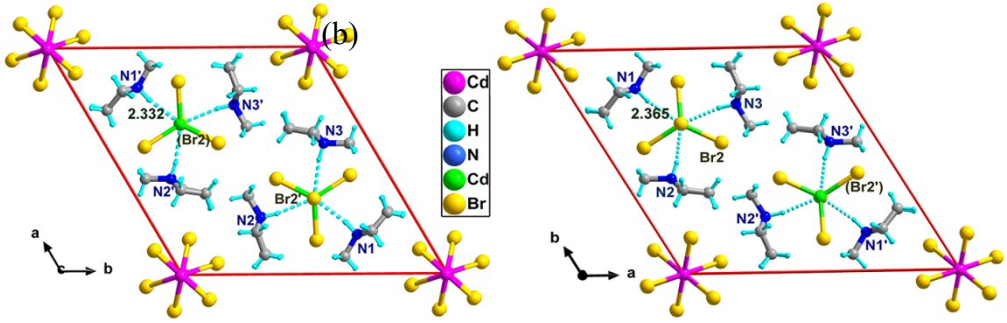

Figure S9. The packing diagram structures of **3** at 343 (a) and 253 (b) K. The dashed lines denote the N-H···Br interactions. The hydrogen atoms of C atoms are omitted for clarity. Thermal ellipsoids for all atoms are shown at 30% probability level.

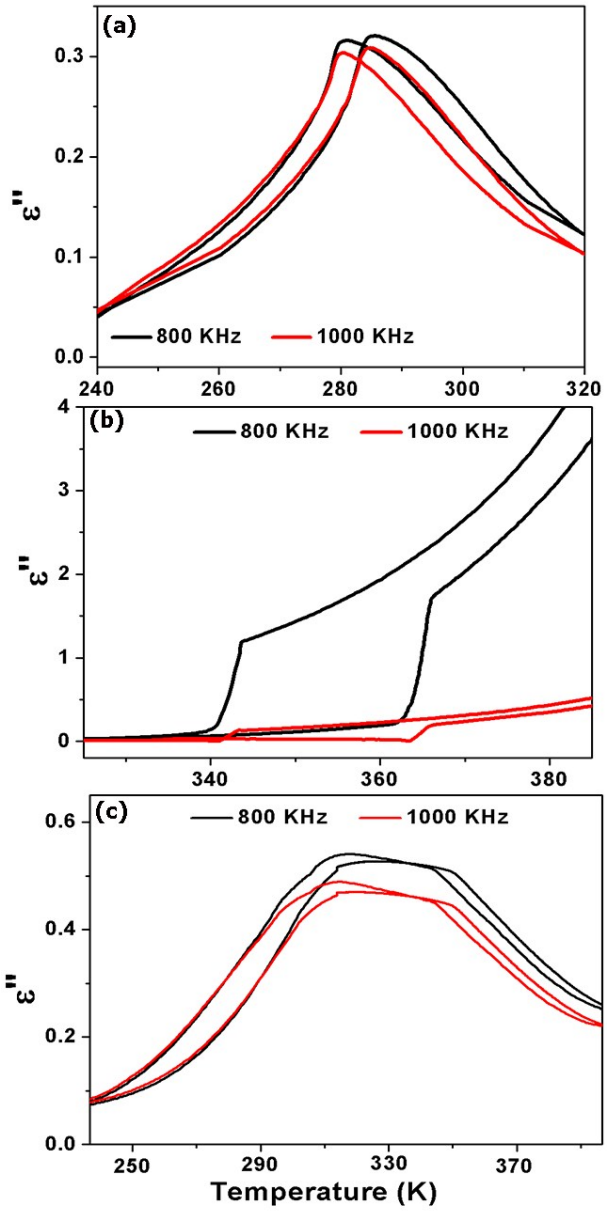

Figure S10. Imaginary part of dielectric constants (ε'') of the dielectric permittivity of **1** (a), **2** (b) and **3** (c) at selected frequencies on heating and cooling runs.

Table S1. Crystal data and structure refinements for **1**, **2** and **3**.

moiety formula	$(C_5H_{12}N)CdBr_3$		$(C_5H_{12}N)_2CdBr_4$		$(C_5H_{12}N)_3CdBr_3{\cdot}CdBr_4$	
T (K)	293	263	373	293	343	253
*F*w	438.27	438.27	604.32	605.1	1042.59	1042.59
Space group	*Pnma*	$P2_1/c$	*Pbca*	*Pbca*	*P*-3	*P*-3
Z	4	4	8	8	2	2
a(Å)	15.322 (4)	6.977 (1)	12.421(7)	12.409 (2)	15.553(1)	15.358 (2)
b(Å)	7.0479 (1)	15.04 (3)	13.319(7)	13.230 (1)	15.553(1)	15.358 (2)
c(Å)	10.105 (4)	12.106 (2)	24.209(1)	23.79 (3)	7.117(8)	7.0766 (1)
V (Å^3)	1091.2(6)	1055(3)	4005(4)	3906(8)	1491(3)	1445.5(5)
T_{min} /T_{max}	0.077/0.212	0.070/0.201	0.154/0.337	0.205/0.395	0.111/0.273	0.103/0.262
F(000)	808	808	2288	2290	976	976

R_{int}	0.093	0.043	0.315	0.099	0.072	0.064
GOF	1.04	1.09	1.13	1.1	1.02	0.97
$R1/wR2[I > 2\sigma(I)]$	0.054/0.12	0.118/0.340	0.148/0.349	0.062/0.151	0.033/0.071	0.027/0.052

Table S2 Selected bond lengths [Å] and angles [°] for **1** at 293 and 263 K.

HTP(293 K)	Cd1—Br2	2.7709 (1)
	Cd1—Br1	2.7829 (1)
	Cd1—Br3i	2.8055 (1)
	Br1—Cd1ii	2.7829 (1)
	Br2—Cd1—Br2i	180
	Br2—Cd1—Br1	95.86 (5)
	Br2i—Cd1—Br1	84.14 (5)
	Br2—Cd1—Br1i	84.14 (5)
	Br2i—Cd1—Br1i	95.86 (5)
	Br1—Cd1—Br1i	180
	Br2—Cd1—Br3i	94.97 (5)
	Br2i—Cd1—Br3i	85.03 (5)
	Br1—Cd1—Br3i	83.63 (5)
	Br1i—Cd1—Br3i	96.37 (5)
	Br2—Cd1—Br3	85.04 (5)
	Br2i—Cd1—Br3	94.96 (5)
	Br1—Cd1—Br3	96.37 (5)
	Br1i—Cd1—Br3	83.63 (5)
	Br3i—Cd1—Br3	180
	Cd1—Br1—Cd1ii	78.56 (5)
	Cd1—Br2—Cd1iii	78.97 (5)
	Cd1iii—Br3—Cd1	77.81 (4)
LTP(263 K)	Cd1—Br3	2.753 (5)
	Cd1—Br2	2.758 (5)
	Cd1—Br4	2.779 (4)
	Cd2—Br3	2.737 (5)
	Cd2—Br2	2.754 (4)
	Cd2—Br4	2.786 (5)
	Br3—Cd1—Br3iv	180
	Br3—Cd1—Br2iv	95.56 (2)
	Br3iv—Cd1—Br2iv	84.44 (2)
	Br3—Cd1—Br2	84.44 (2)
	Br3iv—Cd1—Br2	95.56 (2)
	Br2iv—Cd1—Br2	180.00 (1)
	Br3—Cd1—Br4	84.75 (1)
	Br3iv—Cd1—Br4	95.25 (1)
	Br2iv—Cd1—Br4	96.44 (2)
	Br2—Cd1—Br4	83.56 (2)
	Br3—Cd1—Br4iv	95.25 (1)

	Br3iv—Cd1—Br4iv	84.75 (1)
	Br2iv—Cd1—Br4iv	83.56 (2)
	Br2—Cd1—Br4iv	96.44 (2)
	Br4—Cd1—Br4iv	180
	Br3—Cd2—Br3v	180
	Br3—Cd2—Br2v	95.18 (1)
	Br3v—Cd2—Br2v	84.81 (1)
	Br3—Cd2—Br2	84.82 (1)
	Br3v—Cd2—Br2	95.19 (1)
	Br2v—Cd2—Br2	180.00 (1)
	Br3—Cd2—Br4	84.92 (2)
	Br3v—Cd2—Br4	95.08 (2)
	Br2v—Cd2—Br4	96.51 (1)
	Br2—Cd2—Br4	83.50 (1)
	Br3—Cd2—Br4v	95.08 (2)
	Br3v—Cd2—Br4v	84.92 (2)
	Br2v—Cd2—Br4v	83.50 (1)
	Br2—Cd2—Br4v	96.50 (1)
	Br4—Cd2—Br4v	180
	Cd2—Br2—Cd1	78.53 (2)
	Cd2—Br3—Cd1	78.91 (2)
	Cd1—Br4—Cd2	77.65 (2)

Symmetry codes: (i) *x, y*+1, *z*+1*;* (ii) *x, y*-1, *z*+1*;* (iii) *x, y, z*+1*;* (iv) *x, y*+2, *z*
(iv) *x, y,* z+1*;* (vi) *x*+1, *y, z*+1

Table S3 Selected bond lengths [Å] and angles [°] for **2** at 373 and 293 K.

HTP(373 K）	Cd1—Br4	2.554 (4)
	Cd1—Br2	2.564 (4)
	Cd1—Br1	2.576 (4)
	Cd1—Br3	2.615 (5)
	Br4—Cd1—Br2	113.11 (2)
	Br4—Cd1—Br1	112.79 (2)
	Br2—Cd1—Br1	108.02 (1)
	Br4—Cd1—Br3	107.21 (2)
	Br2—Cd1—Br3	104.74 (2)
	Br1—Cd1—Br3	110.69 (1)
ITP(293 K)	Cd1—Br2	2.576 (4)
	Cd1—Br3	2.587 (2)
	Cd1—Br1	2.633 (3)
	Br4—Cd1—Br2	114.47 (8)
	Br4—Cd1—Br3	113.31 (9)
	Br2—Cd1—Br3	107.37 (6)
	Br4—Cd1—Br1	105.81 (5)

	Br2—Cd1—Br1	104.25 (7)
	Br3—Cd1—Br1	111.30 (5)

Table S4 Hydrogen-Bond Geometry (Å, deg) for the N–H···Br interactions at 293K in **2**.

		D—H	H...A	D...A	D—H...A
ITP(293 K)	N2—H2...Br1i	0.98	2.52	3.491 (1)	171.2

Symmetry codes: (i) *x, y*+1, *z*

Table S5 Selected bond lengths [Å] and angles [°] for **3** at 343 and 253 K.

HTP(343 K)	Cd1—Br1	2.8067 (2)
	Cd2—Br1	2.8075 (2)
	Cd3—Br3	2.560 (2)
	Cd3—Br2	2.736 (3)
	Br1i—Cd1—Br1	180
	Br1i—Cd1—Br1ii	84.12 (6)
	Br1—Cd1—Br1ii	95.88 (6)
	Br1i—Cd1—Br1iii	95.88 (6)
	Br1—Cd1—Br1iii	84.12 (6)
	Br1ii—Cd1—Br1iii	180
	Br1i—Cd1—Br1iv	95.88 (6)
	Br1—Cd1—Br1iv	84.12 (6)
	Br1ii—Cd1—Br1iv	95.88 (6)
	Br1iii—Cd1—Br1iv	84.12 (6)
	Br1i—Cd1—Br1v	84.12 (6)
	Br1—Cd1—Br1v	95.88 (6)
	Br1ii—Cd1—Br1v	84.12 (6)
	Br1iii—Cd1—Br1v	95.88 (6)
	Br1iv—Cd1—Br1v	180
	Br1vi—Cd2—Br1	180
	Br1vi—Cd2—Br1vii	84.09 (6)
	Br1—Cd2—Br1vii	95.90 (6)
	Br1vi—Cd2—Br1iii	95.91 (6)
	Br1—Cd2—Br1iii	84.10 (6)
	Br1vii—Cd2—Br1iii	180.00 (3)
	Br1vi—Cd2—Br1iv	95.91 (6)
	Br1—Cd2—Br1iv	84.09 (6)
	Br1vii—Cd2—Br1iv	95.91 (6)
	Br1iii—Cd2—Br1iv	84.09 (6)
	Br1vi—Cd2—Br1viii	84.09 (6)
	Br1—Cd2—Br1viii	95.91 (6)
	Br1vii—Cd2—Br1viii	84.09 (6)
	Br1iii—Cd2—Br1viii	95.91 (6)
	Br1iv—Cd2—Br1viii	180
	Br3ix—Cd3—Br3	115.32 (2)
	Br3ix—Cd3—Br3x	115.32 (2)

	Br3—Cd3—Br3x	115.32 (2)
	Br3ix—Cd3—Br2	102.68 (3)
	Br3—Cd3—Br2	102.68 (3)
	Br3x—Cd3—Br2	102.68 (3)
	Cd1—Br1—Cd2	78.67 (8)
LTP(253 K)	Cd1—Br1	2.7940 (6)
	Cd2—Br1	2.7937 (6)
	Cd3—Br3	2.5552 (6)
	Cd3—Br2	2.7347 (1)
	Br1i—Cd1—Br1ii	84.170 (2)
	Br1i—Cd1—Br1iii	95.830 (2)
	Br1ii—Cd1—Br1iii	180.000 (2)
	Br1i—Cd1—Br1iv	95.830 (2)
	Br1ii—Cd1—Br1iv	95.830 (2)
	Br1iii—Cd1—Br1iv	84.170 (2)
	Br1i—Cd1—Br1	180
	Br1ii—Cd1—Br1	95.830 (2)
	Br1iii—Cd1—Br1	84.170 (2)
	Br1iv—Cd1—Br1	84.170 (2)
	Br1i—Cd1—Br1v	84.170 (2)
	Br1ii—Cd1—Br1v	84.170 (2)
	Br1iii—Cd1—Br1v	95.830 (2)
	Br1iv—Cd1—Br1v	180.000 (2)
	Br1—Cd1—Br1v	95.830 (2)
	Br1iv—Cd2—Br1vi	95.82 (2)
	Br1iv—Cd2—Br1iii	84.18 (2)
	Br1vi—Cd2—Br1iii	180
	Br1iv—Cd2—Br1vii	95.82 (2)
	Br1vi—Cd2—Br1vii	84.18 (2)
	Br1iii—Cd2—Br1vii	95.82 (2)
	Br1iv—Cd2—Br1viii	180
	Br1vi—Cd2—Br1viii	84.181 (2)
	Br1iii—Cd2—Br1viii	95.82 (2)
	Br1vii—Cd2—Br1viii	84.18 (2)
	Br1iv—Cd2—Br1	84.18 (2)
	Br1vi—Cd2—Br1	95.82 (2)
	Br1iii—Cd2—Br1	84.18 (2)
	Br1vii—Cd2—Br1	180
	Br1viii—Cd2—Br1	95.82 (2)
	Cd2—Br1—Cd1	78.578 (2)
	Br3ix—Cd3—Br3x	115.484 (2)
	Br3ix—Cd3—Br3	115.485 (2)
	Br3x—Cd3—Br3	115.483 (2)
	Br3ix—Cd3—Br2	102.45 (2)
	Br3x—Cd3—Br2	102.45 (2)
	Br3—Cd3—Br2	102.45 (2)

Symmetry codes: HTP (i) *x*, *y*+2, *z*+2; (ii) *x*+1, *y*+1, *z*+2; (iii) *x*-1, *y*+1, *z* ; (iv) *x*+1, *y*+2,

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

Table S6 Hydrogen-Bond Geometry (Å, deg) for the weak N–H···Br interactions at 343 K and 253 K in **3**.

		D—H	H...A	D...A	D—H...A
HTP(343 K)	N1—H1...Br2i	0.98	2.36	3.331 (6)	168.6
LTP(253 K)	N1—H1...Br2	0.98	2.33	3.294 (4)	167

Symmetry codes: (i) *x*+1, *y*+1, *z*+1.