Supporting Information

Halogen substitution regulates the phase transition temperature and band gap of semiconductor compounds

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Experimental section

Preparation of crystals

All solvent and reagents were purchased from commercial sources and used without any further purification. $(CH_3CH_2NH_3)_3BiCl_6$ (**1**) and $(CH_3CH_2NH_3)_3BiBr_6$ (**2**) were obtained by slowly evaporating corresponding acid solution (about 20 ml) containing ethylamine hydrochloride (3 mol), bismuth chloride (1 mol for **1**) and bismuth bromide (1 mol for **2**) on a drying heating table at 40 °C for few days. $(CH_2ClCH_2NH_3)_3BiCl_6$ (**3**) and $(CH_2ClCH_2NH_3)_3BiBr_6$ (**4**) were obtained by slowly evaporating corresponding acid solution (about 20 ml) containing 2-chloroethylamine hydrochloride, (3 mol), bismuth chloride (1 mol for **3**) and bismuth bromide (1 mol for **4**) on a drying heating table at 40 °C for few days.

Single-crystal X-ray crystallography

Temperature-dependent X-ray diffraction data of four compounds were collected at different temperatures on a Rigaku Saturn 724 diffractometer with Mo Kα radiation (λ = 0.71073). The Crystal-Clear software package (Rigaku, 2005) is used to perform data reduction and multi-scan absorption correction. Crystal-clear software package has been processed all data processing including empirical absorption correction. The crystal structure was solved by direct method, and then refined by using SHELXLTL software package (SHELX-14) in F^2 using full matrix least squares refinement. By suing Uiso(H)=1.2 Ueq (C and N) riding model, all H atoms are generated geometrically and refined, all reflective anisotropic goblins producing non H atoms using $I > 2\sigma(I)$. The non-hydrogen atoms are anisotropically refined, and all H atoms are placed at ideal positions. The molecular structures and the packing views with DIAMOND (Brandenburg and Putz, 2005). A summary of the crystallographic data and structural refinement details of the four compounds **1**, **2**, **3**, and **4** is given in

Tables S1 and S2, respectively.

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO X-ray diffractometer for the four compounds. Record diffraction pattern in the 2θ range of 2-50° in steps of 0.02°.

DSC, Dielectric properties and TGA measurements

Differential scanning calorimetry experiments were carried out on a PerkinElmer Diamond DSC instrument by heating and cooling polycrystalline sample were placed in aluminum crucibles with a rate of 5k/min under the nitrogen atmosphere. power-pressed pellets of the polycrystalline samples deposited with carbon conducting glue were as electrodes for the measurement of dielectric constant. Measurement of Complex permittivity was performed on TongHui TH2828A apparatus in the special temperature range at selected frequencies with an applied electric field of 1V. Thermogravimetric analyses (TGA) were carried out on a TA Q50 system with a heating rate of 10 K min^{-1} under a nitrogen atmosphere.

Absorption spectrum

Ultraviolet-vis diffuse reflectance spectra of four compounds were performed by using a Shimadzu UV-2450 spectrophotometer operating in the range of 200 to 900 nm at room temperature .Use barium sulfate ($BaSO_4$) plate as standard (100%) Reflectance, which is coated with a finely ground sample from the crystal of **1**, **2** ,**3** and **4** were prepared for measurement. The absorption spectrum is calculated from the reflectance spectrum using the Kubelka-Munk equation: $F(R_\infty) = (1-R_\infty)^2 / (2R_\infty)$, which can be used to evaluate the optical band gap (E_g) of the material. The $E_g$can be determined from the variant of the *Tauc* function:

$$(hv \cdot F(R_\infty))^2 = A(hv - E_g)$$

in which h is planck's constant, v denotes the frequency of vibration, $F(R_\infty)$ representatives the Kubelka -Munk equation. A is the proportional constant. The value of the exponent n denotes the nature of the sample's transition. n=1/2 for direct allowed transition and n=2 for indirect allowed transition. Therefore, the optical band gap E_g of four compounds can be determined by plotting $(hv.F(R_\infty))^{1/n}$ against the energy in electron volts and extrapolation of intercept from linear region to X-axis.

Theoretical Calculation

The exchange-correlation functional was described by a generalized gradient approximation (GGA) with Perdew−Burke−Ernzerhof functional for solids (PBEsol) scheme. The interactions between the ionic cores and the electrons were described by the OTFG norm conserving pseudopotential. The following orbital electrons were treated as valence electrons: $H1s^1$, $C2s^22p^2$, $N2s^22p^3$, $Cl3s^23p^5$,$Bi6s^26p^3$. a Monkhorst - Pack k-point sampling of 2×1×1 and an energy cutoff adopted 898 eV.

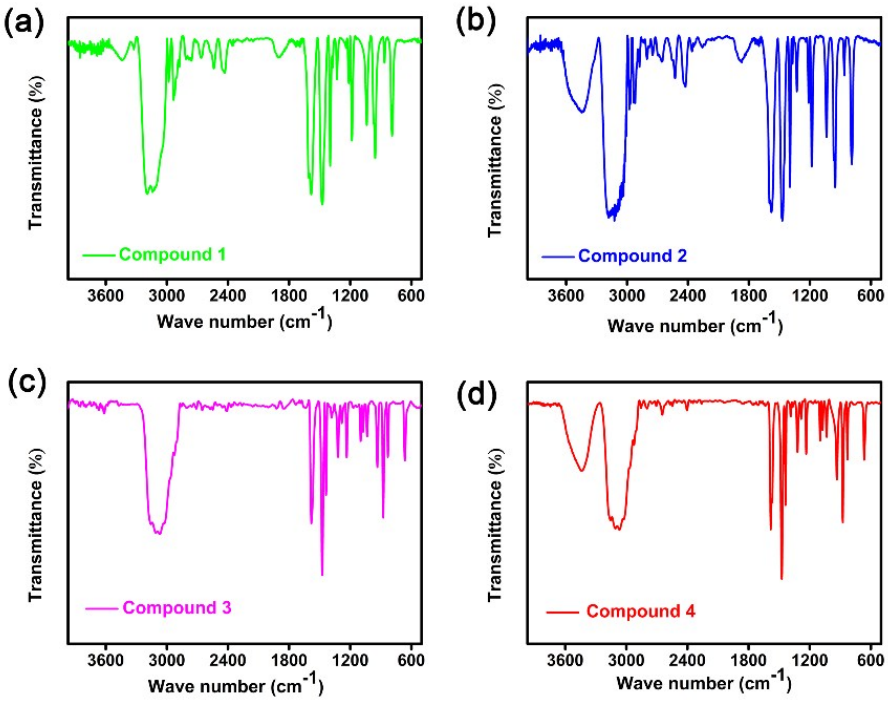

Fig. S1 IR spectrum of **1** (a), **2** (b), **3** (c) and **4** (d)in a KBr-kiluted at room temperature.

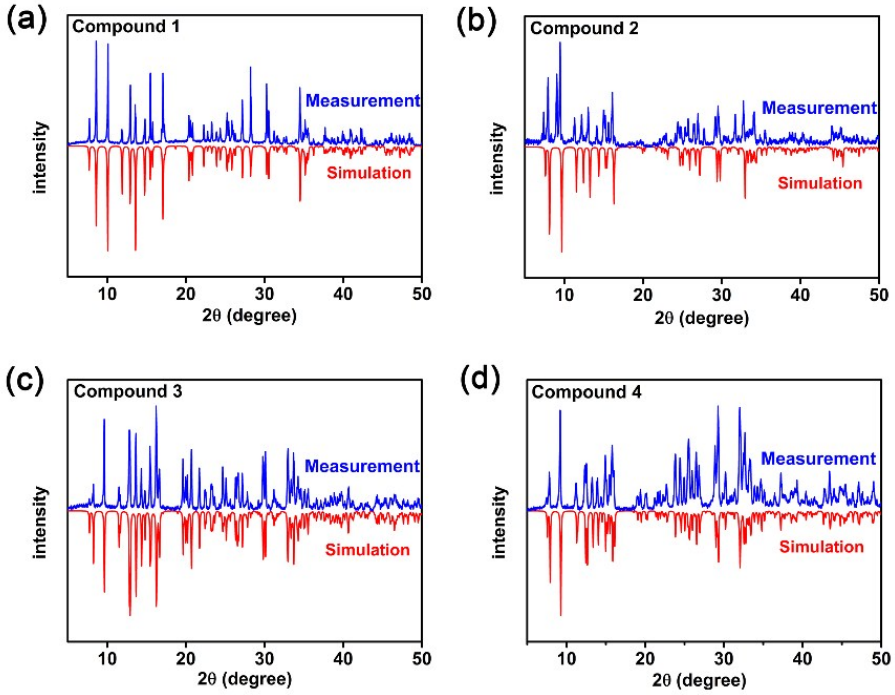

Fig. S2 Powder X-ray diffraction patterns for **1** (a), **2** (b), **3** (c) and **4** (d) at 293 K, verifying the purify of the bulk phases.

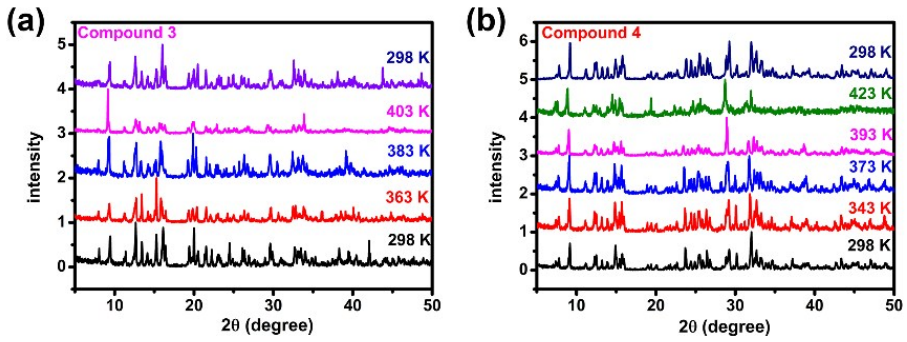

Fig. S3 Variable-temperature PXRD patterns of compounds **3** (a) and **4** (b).

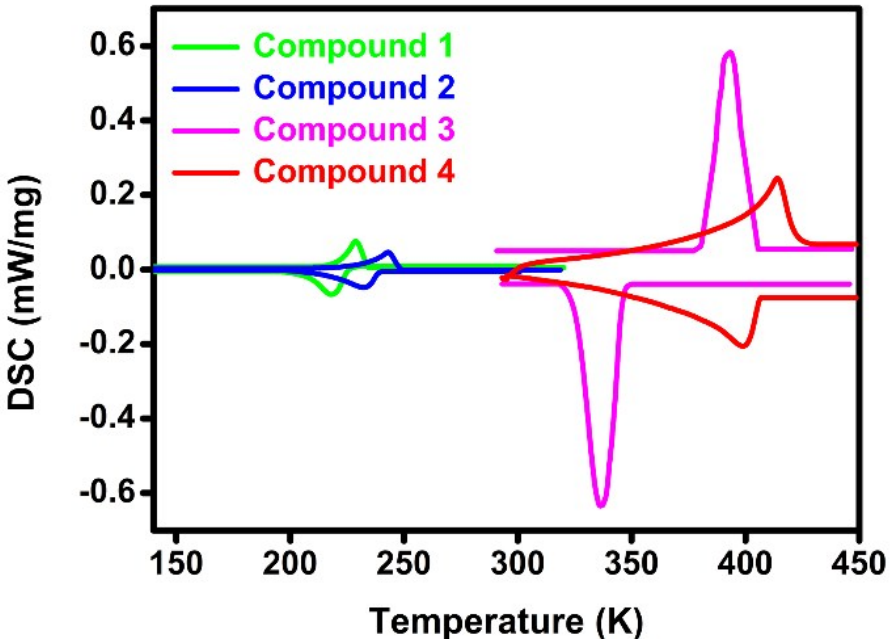

Fig. S4 DSC curves in a heating-cooling cycle for polycrystalline samples of compounds **1**, **2**, **3**, and **4**, respectively.

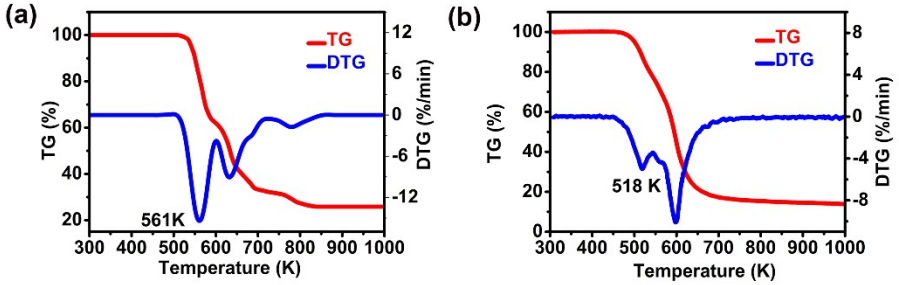

Fig. S5 (a) TGA curve and DTG curve of **3**. (b) TGA curve and DTG curve of **4**.

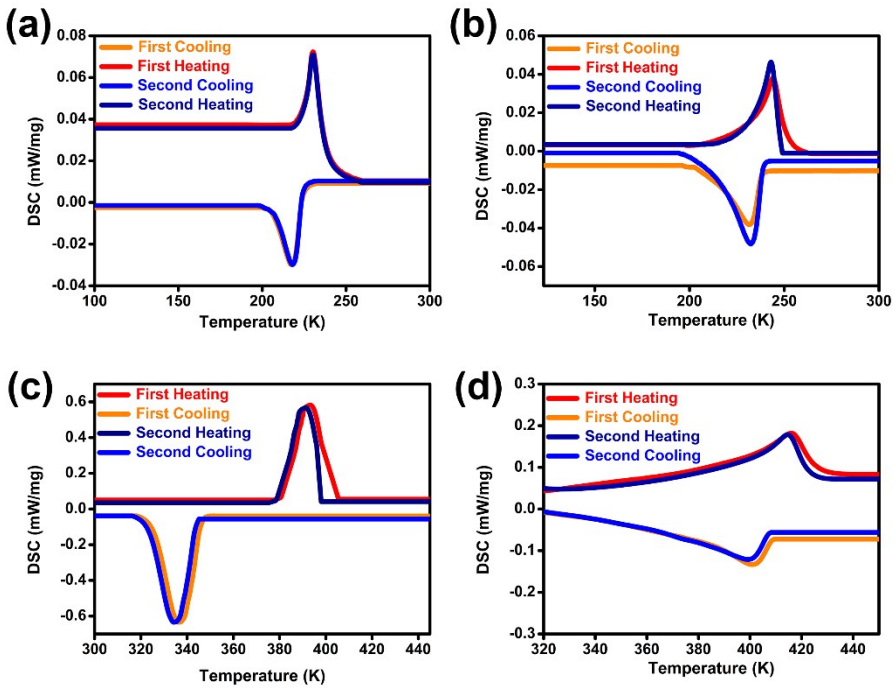

Fig. S6 DSC curves in two heating-cooling cycles for polycrystalline samples of compounds **1** (a), **2** (b), **3** (c), and **4** (d), respectively.

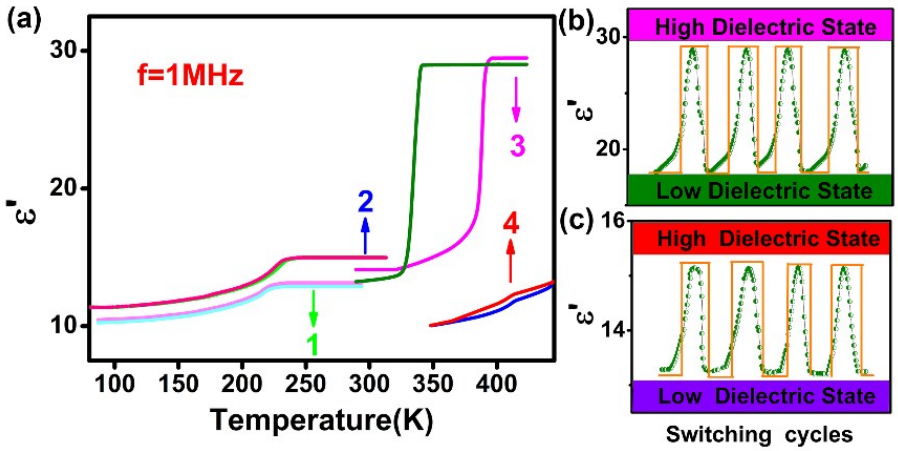

Fig. S7 (a) Temperature-dependent real part (ε′) of the dielectric constant measured at 1MHz for four compounds. The ε′-switching at a frequency of 1 MHz for **3** (b) and **4** (c).

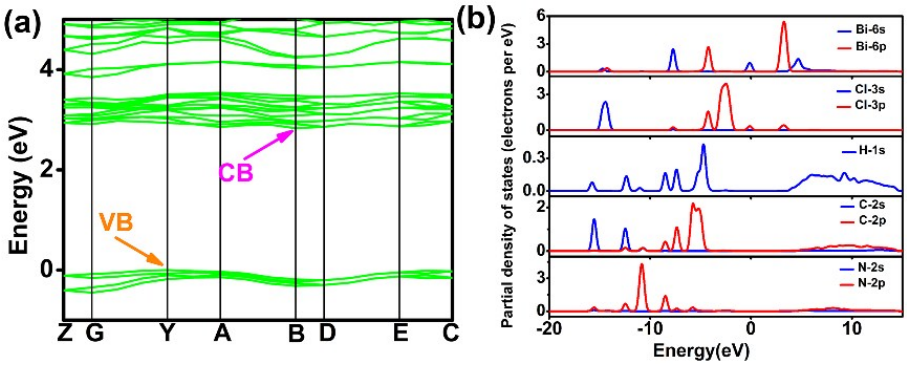

Fig. S8 Calculated band structure (a) and PDOS (b) of compound **1**.

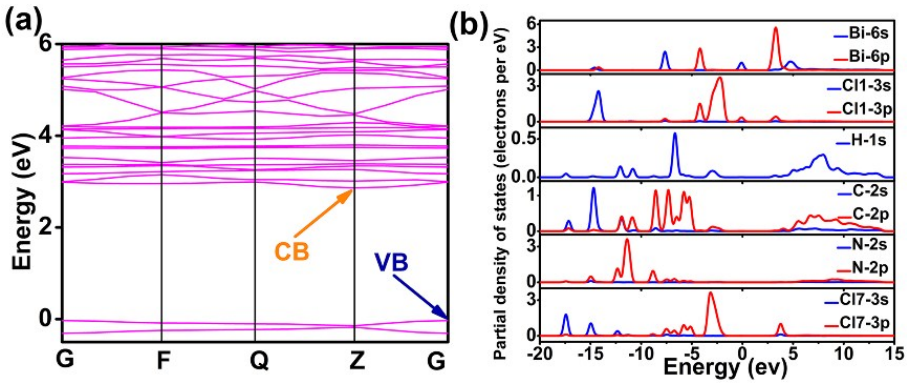

Fig. S9 Calculated band structure (a) and PDOS (b) of compound **3**.

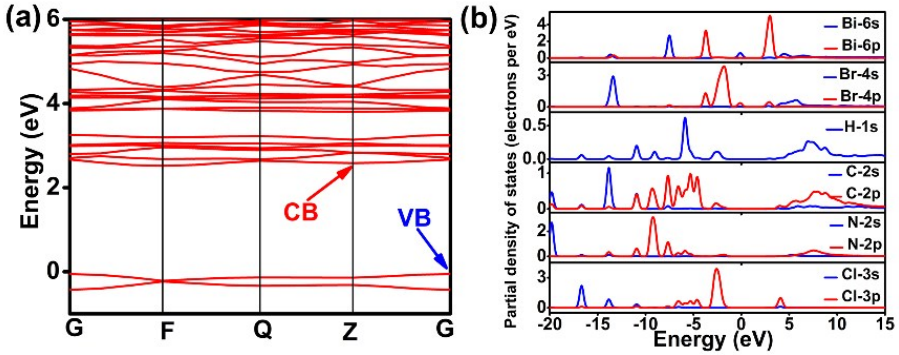

Fig. S10 Calculated band structure (a) and PDOS (b) of compound **4**.

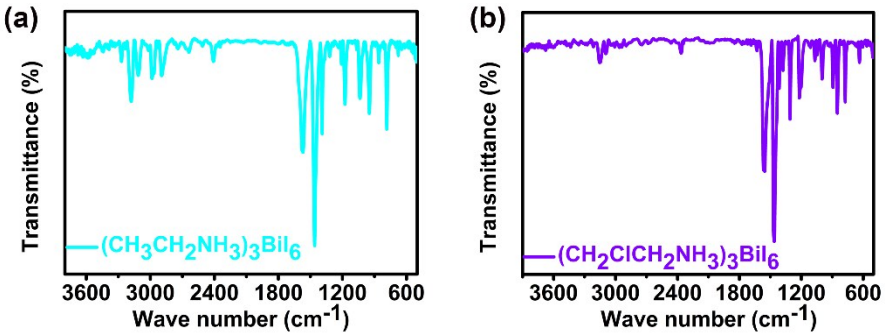

Fig. S11 IR spectrum of $(CH_3CH_2NH_3)_3BiI_6$ (a) and $(CH_2ClCH_2NH_3)_3BiI_6$ (b) in a KBr-kiluted at room temperature.

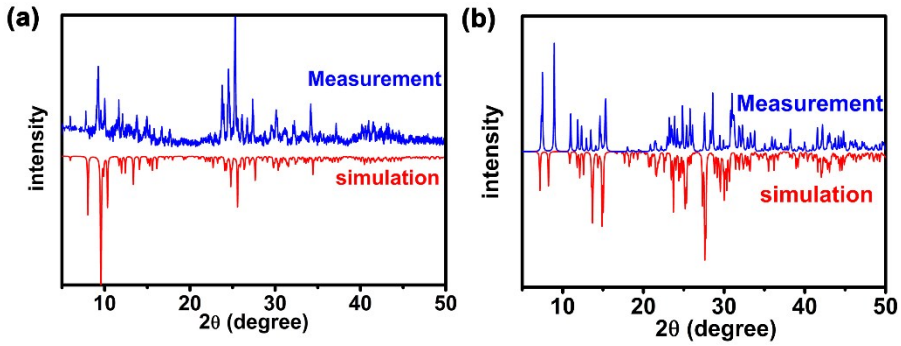

Fig. S12 Powder X-ray diffraction patterns for $(CH_3CH_2NH_3)_3BiI_6$ (a) and $(CH_2ClCH_2NH_3)_3BiI_6$ (b) at 293 K, verifying the purify of the bulk phases.

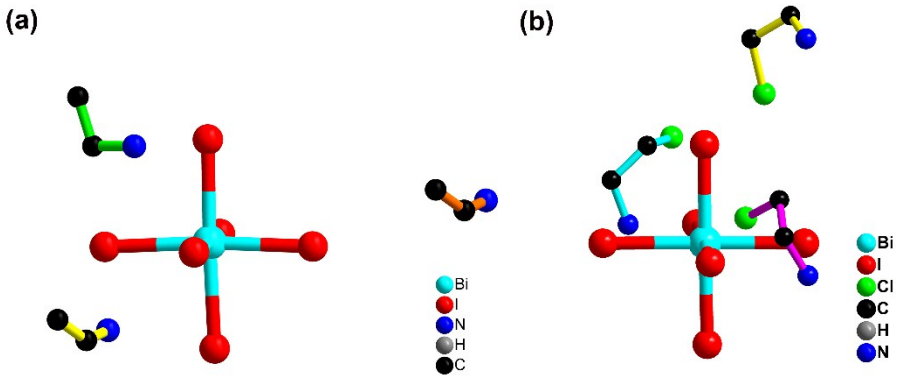

Fig. S13 Molecular structure of $(CH_3CH_2NH_3)_3BiI_6$ at 293 K (a) and Molecular structure of $(CH_2ClCH_2NH_3)_3BiI_6$ at 293 K (b).

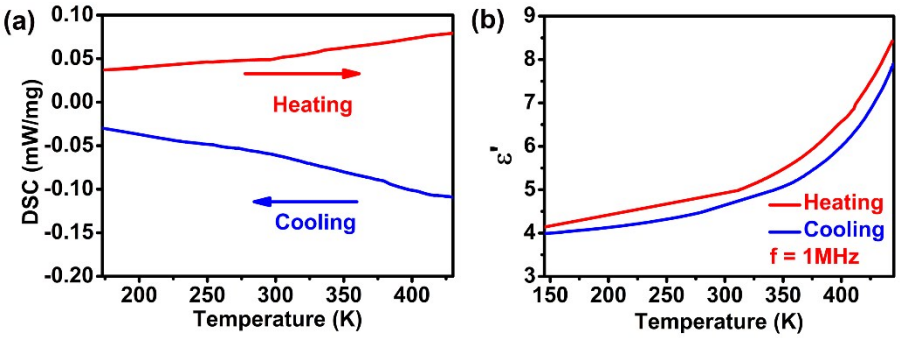

Fig. S14 (a) DSC curves in a heating-cooling cycle for polycrystalline samples of compounds $(CH_3CH_2NH_3)_3BiI_6$. (b) Temperature-dependent real part (ε′) of the dielectric constant measured at 1MHz for $(CH_3CH_2NH_3)_3BiI_6$.

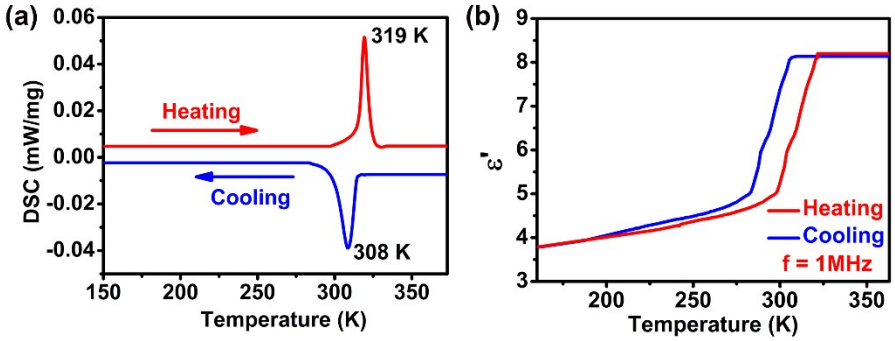

Fig. S15 (a) DSC curves in a heating-cooling cycle for polycrystalline samples of compounds $(CH_2ClCH_2NH_3)_3BiI_6$. (b) Temperature-dependent real part (ε′) of the dielectric constant measured at 1MHz for $(CH_2ClCH_2NH_3)_3BiI_6$.

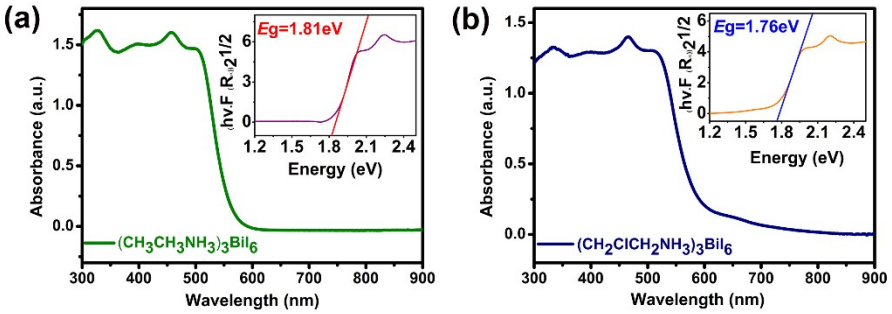

Fig. S16 (a) UV−vis absorption spectra of $(CH_3CH_2NH_3)_3BiI_6$. The inset shows the Tauc plot with an estimated bandgap of 1.81 eV. (b) UV−vis absorption spectra of $(CH_2ClCH_2NH_3)_3BiI_6$. The inset shows the Tauc plot with an estimated bandgap of 1.76 eV.

Table S1. Crystal data, data collection and reduction parameters of crystals **1** and **2**.

	1 (170 K)	**1** (293 K)	**2** (170 K)	**2** (293 K)
Empirical formula	$C_6H_{24}BiCl_6N_3$	$C_6H_{24}BiCl_6N_3$	$C_6H_{24}BiBr_6N_3$	$C_6H_{24}BiBr_6N_3$
Formula weight	559.96	559.96	826.66	826.66
Crystal system,	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*P*2/*c*	*C*2/*m*	*P*2/*c*	*C*2/*m*
Radiation type	MoKα (0.71073 Å)	MoKα (0.71073 Å)	MoKα (0.71073 Å)	MoKα (0.71073 Å)
Temperature/K	170	293	170	293
a / Å	11.5267 (3)	21.1620 (15)	11.7730 (3)	22.444 (3)
b / Å	7.8653 (2)	7.9735 (5)	8.0673 (2)	8.1886 (8)
c / Å	21.5333 (5)	11.8046(7)	22.7281 (6)	11.9852 (14)
α / deg	90	90	90	90
β / deg	103.831(2)	104.186(7)	103.720(2)	104.248(13)
γ / deg	90	90	90	90
Volume / Å^3	1895.62 (8)	1931.1 (2)	2097.04(9)	2134.9 (4)
Z	4	4	4	4
D_x(g cm^{-3})	1.962	1.926	2.618	2.572
F (000)	1064	1064	1496	1496
Goodness-of-fit on F^2	1.07	1.05	1.03	1.03
R_{int}	0.036	0.040	0.047	0.064
R_1 / wR_2 [$I > 2\sigma(I)$]	0.028 / 0.068	0.058 / 0.143	0.069/0.183	0.060/ 0.165
No. of reflections	6463	2959	7102	2025
No. of parameters	151	90	151	84

Table S2. Crystal data, data collection and reduction parameters of crystals **3** and **4**.

	3 (295 K)	**3** (403 K)	**4** (289 K)	**4** (420 K)
Empirical formula	$C_6H_{21}BiCl_9N_3$	$C_6H_{21}BiCl_9N_3$	$C_6H_{21}BiBr_6Cl_3N_3$	$C_6H_{21}BiBr_6Cl_3N_3$
Formula weight	663.29	663.29	929.99	929.99
Crystal system,	Triclinic	Monoclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	*C*2/*m*	$P\bar{1}$	*C*2/*m*
Radiation type	MoKα (0.71073 Å)	MoKα (0.71073 Å)	MoKα (0.71073 Å)	MoKα (0.71073 Å)
Temperature/K	295	403	289	420
a / Å	8.1810(2)	22.520(2)	8.3218(2)	24.290(2)
b / Å	11.7216(4)	8.2945(5)	12.1968(3)	8.2740(7)

c / Å	11.8724(3)	12.1353(11)	12.2353(4)	12.4821(9)
α / deg	104.188(2)	90	104.697(2)	90
β / deg	93.217(2)	106.123(9)	108.110(2)	108.894(7)
γ / deg	108.402(3)	90	93.253(2)	90
Volume / Å^3	1036.24(5)	2177.6(3)	1129.25(6)	2373.4(3)
Z	2	4	2	4
D_x(g cm^{-3})	2.126	2.023	2.735	2.603
F (000)	628.0	1256	844.0	1688
Goodness-of-fit on F^2	1.01	1.05	1.03	0.96
R_{int}	0.049	0.067	0.036	0.054
R_1 / wR_2 [$I > 2\sigma(I)$]	0.040 / 0.092	0.062/0.214	0.046 / 0.114	0.060/0197
No. of reflections	6989	2068	7521	3636
No. of parameters	175	131	176	122

Table S3. Selected bond lengths [Å] and angles [°] for **1**.

170 K			
Bi1—Cl1	2.6242 (9)	Cl1—Bi1—Cl6	90.35 (3)
Bi1—Cl6	2.6911 (9)	Cl1—Bi1—Cl4	89.34 (3)
Bi1—Cl4	2.6920 (9)	Cl6—Bi1—Cl4	91.25 (3)
Bi1—Cl5	2.7229 (9)	Cl1—Bi1—Cl5	91.88 (3)
Bi1—Cl8	2.7427 (8)	Cl6—Bi1—Cl5	90.78 (3)
Bi1—Cl7	2.8133 (9)	Cl4—Bi1—Cl5	177.62 (3)
		Cl1—Bi1—Cl8	90.54 (3)
		Cl6—Bi1—Cl8	178.30 (3)
		Cl4—Bi1—Cl8	90.21 (3)
		Cl5—Bi1—Cl8	87.74 (3)
		Cl1—Bi1—Cl7	175.68 (3)
		Cl6—Bi1—Cl7	88.70 (3)
		Cl4—Bi1—Cl7	94.89 (3)
		Cl5—Bi1—Cl7	83.92 (3)
		Cl8—Bi1—Cl7	90.31 (3)
293 K			
Bi1—Cl5	2.611 (4)	Cl5—Bi1—Cl1	90.12 (12)
Bi1—Cl1	2.654 (2)	Cl5—Bi1—Cl1^i	90.12 (12)
Bi1—Cl1^i	2.654 (2)	Cl1—Bi1—Cl1^i	93.16 (13)
Bi1—Cl2	2.745 (3)	Cl5—Bi1—Cl2	91.26 (13)
Bi1—Cl2^i	2.745 (3)	Cl1—Bi1—Cl2	88.59 (11)
Bi1—Cl4	2.756 (4)	Cl1^i—Bi1—Cl2	177.77 (9)
		Cl5—Bi1—Cl2^i	91.26 (13)

		Cl1—Bi1—Cl2^{i}	177.77 (9)
		Cl1^{i}—Bi1—Cl2^{i}	88.59 (11)
		Cl2—Bi1—Cl2^{i}	89.62 (15)
		Cl5—Bi1—Cl4	178.27 (14)
		Cl1—Bi1—Cl4	91.06 (9)
		Cl1^{i}—Bi1—Cl4	91.06 (9)
		Cl2—Bi1—Cl4	87.52 (11)
		Cl2^{i}—Bi1—Cl4	87.52 (11)

Symmetry codes: (i) x, $-y$, z in 293 K.

Table S4. Selected bond lengths [Å] and angles [°] for **2**.

170 K			
Bi1—Br7	2.7816 (10)	Br7—Bi1—Br6	90.29 (3)
Bi1—Br6	2.8376 (8)	Br7—Bi1—Br4	90.87 (3)
Bi1—Br4	2.8386 (9)	Br6—Bi1—Br4	90.44 (3)
Bi1—Br2	2.8833 (9)	Br7—Bi1—Br2	92.52 (3)
Bi1—Br5	2.8922 (9)	Br6—Bi1—Br2	176.59 (3)
Bi1—Br3	2.9506 (9)	Br4—Bi1—Br2	91.46 (3)
		Br7—Bi1—Br5	90.96 (3)
		Br6—Bi1—Br5	89.61 (3)
		Br4—Bi1—Br5	178.17 (3)
		Br2—Bi1—Br5	88.40 (3)
		Br7—Bi1—Br3	177.17 (3)
		Br6—Bi1—Br3	92.26 (3)
		Br4—Bi1—Br3	87.88 (3)
		Br2—Bi1—Br3	84.98 (3)
		Br5—Bi1—Br3	90.29 (3)
293 K			
Bi1—Br5	2.772 (3)	Br5—Bi1—Br1	90.69 (6)
Bi1—Br1	2.8101 (17)	Br5—Bi1—Br1^{i}	90.69 (6)
Bi1—Br1^{i}	2.8101 (17)	Br1—Bi1—Br1^{i}	91.64 (8)
Bi1—Br2	2.9015 (18)	Br5—Bi1—Br2	91.39 (7)
Bi1—Br2^{i}	2.9015 (18)	Br1—Bi1—Br2	89.39 (6)
Bi1—Br4	2.915 (3)	Br1^{i}—Bi1—Br2	177.67 (6)
		Br5—Bi1—Br2^{i}	91.39 (7)
		Br1—Bi1—Br2^{i}	177.67 (6)
		Br1^{i}—Bi1—Br2^{i}	89.39 (6)
		Br2—Bi1—Br2^{i}	89.51 (8)
		Br5—Bi1—Br4	178.35 (8)
		Br1—Bi1—Br4	90.46 (6)
		Br1^{i}—Bi1—Br4	90.46 (6)
		Br2—Bi1—Br4	87.44 (6)

		$Br2^{i}$—Bi1—Br4	87.44 (6)

Symmetry codes: (i) *x*, −*y*, *z* in 293 K.

Table S5. Selected bond lengths [Å] and angles [°] for **3**.

295 K			
Bi1—Cl2	2.6356 (15)	Cl2—Bi1—Cl3	90.05 (6)
Bi1—Cl3	2.6577 (17)	Cl2—Bi1—Cl4	93.31 (5)
Bi1—Cl4	2.7021 (14)	Cl3—Bi1—Cl4	88.90 (5)
Bi1—Cl1	2.7163 (14)	Cl2—Bi1—Cl1	89.16 (6)
Bi1—Cl6	2.7875 (15)	Cl3—Bi1—Cl1	90.53 (6)
Bi1—Cl5	2.7943 (13)	Cl4—Bi1—Cl1	177.47 (5)
		Cl2—Bi1—Cl6	88.56 (6)
		Cl3—Bi1—Cl6	176.35 (4)
		Cl4—Bi1—Cl6	87.80 (5)
		Cl1—Bi1—Cl6	92.83 (5)
		Cl2—Bi1—Cl5	175.39 (5)
		Cl3—Bi1—Cl5	85.98 (5)
		Cl4—Bi1—Cl5	88.97 (5)
		Cl1—Bi1—Cl5	88.53 (5)
		Cl6—Bi1—Cl5	95.54 (4)
403 K			
Bi01—Cl8	2.647 (7)	Cl8—Bi01—$Cl7^{i}$	91.2 (2)
Bi01—$Cl7^{i}$	2.684 (5)	Cl8—Bi01—Cl7	91.2 (2)
Bi01—Cl7	2.684 (5)	$Cl7^{i}$—Bi01—Cl7	89.8 (3)
Bi01—Cl9	2.728 (4)	Cl8—Bi01—Cl9	90.2 (2)
Bi01—$Cl9^{i}$	2.728 (4)	$Cl7^{i}$—Bi01—Cl9	88.7 (2)
Bi01—Cl05	2.763 (9)	Cl7—Bi01—Cl9	178.01 (17)
		Cl8—Bi01—$Cl9^{i}$	90.23 (19)
		$Cl7^{i}$—Bi01—$Cl9^{i}$	178.01 (17)
		Cl7—Bi01—$Cl9^{i}$	88.7 (2)
		Cl9—Bi01—$Cl9^{i}$	92.7 (2)
		Cl8—Bi01—Cl05	178.2 (2)
		$Cl7^{i}$—Bi01—Cl05	87.6 (2)
		Cl7—Bi01—Cl05	87.6 (2)
		Cl9—Bi01—Cl05	90.99 (18)
		$Cl9^{i}$—Bi01—Cl05	90.99 (18)

Symmetry codes: (i) *x*, −*y*+1, *z*; (ii) *x*, −*y*, *z* in 403 K.

Table S6. Selected bond lengths [Å] and angles [°] for **4**.

289 K			
Bi1—Br6	2.7842 (9)	Br6—Bi1—Br4	90.89 (3)
Bi1—Br4	2.8154 (9)	Br6—Bi1—Br5	89.59 (3)

Bi1—Br5	2.8554 (9)	Br4—Bi1—Br5	91.55 (3)
Bi1—Br3	2.8567 (9)	Br6—Bi1—Br3	92.85 (3)
Bi1—Br2	2.9150 (8)	Br4—Bi1—Br3	89.10 (3)
Bi1—Br1	2.9484 (8)	Br5—Bi1—Br3	177.47 (3)
		Br6—Bi1—Br2	88.93 (3)
		Br4—Bi1—Br2	176.68 (3)
		Br5—Bi1—Br2	91.76 (3)
		Br3—Bi1—Br2	87.60 (3)
		Br6—Bi1—Br1	176.16 (3)
		Br4—Bi1—Br1	86.17 (3)
		Br5—Bi1—Br1	88.03 (3)
		Br3—Bi1—Br1	89.57 (3)
		Br2—Bi1—Br1	94.14 (2)
420 K			
Bi01—Br8	2.8062 (19)	Br8—Bi01—Br9	90.44 (5)
Bi01—Br9	2.8465 (15)	Br8—Bi01—Br9^{i}	90.44 (5)
Bi01—Br9^{i}	2.8465 (15)	Br9—Bi01—Br9^{i}	91.79 (7)
Bi01—Br7	2.8775 (16)	Br8—Bi01—Br7	91.51 (5)
Bi01—Br7^{i}	2.8776 (16)	Br9—Bi01—Br7	177.45 (5)
Bi01—Br05	2.915 (2)	Br9^{i}—Bi01—Br7	89.83 (6)
		Br8—Bi01—Br7^{i}	91.51 (5)
		Br9—Bi01—Br7^{i}	89.83 (6)
		Br9^{i}—Bi01—Br7^{i}	177.45 (5)
		Br7—Bi01—Br7^{i}	88.47 (8)
		Br8—Bi01—Br05	178.92 (7)
		Br9—Bi01—Br05	90.31 (5)
		Br9^{i}—Bi01—Br05	90.31 (5)
		Br7—Bi01—Br05	87.71 (5)
		Br7^{i}—Bi01—Br05	87.71 (5)

Symmetry codes: (i) x, $-y+1$, z; (ii) x, $-y$, z in 420 K.

Table S7. Hydrogen-bond parameters (Å, °) for compound **1** at 170 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
170 K				
N2—H1E···Cl6^{i}	0.91	2.44	3.326 (4)	166
N2—H1D···Cl6^{ii}	0.91	2.87	3.429 (4)	121
N2—H1D···Cl4^{iii}	0.91	2.58	3.345 (4)	142
N2—H1C···Cl1^{iii}	0.91	2.66	3.410 (3)	141
N2—H1C···Cl4^{i}	0.91	2.89	3.556 (4)	131
N3—H11C···Cl8^{iv}	0.91	2.40	3.241 (3)	153
N3—H11B···Cl7^{ii}	0.91	2.47	3.195 (3)	137
N3—H11B···Cl4^{iv}	0.91	2.95	3.568 (3)	127

N3—H11A···Cl7	0.91	2.53	3.367 (3)	154
N3—H11A···Cl5	0.91	2.89	3.397 (3)	117
N1—H2C···Cl7^{vi}	0.91	2.23	3.137 (3)	173
N1—H2B···Cl8^{vi}	0.91	2.88	3.516 (3)	128
N1—H2B···Cl8	0.91	2.50	3.190 (3)	133
N1—H2A···Cl5	0.91	2.28	3.181 (4)	169

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

Table S8. Hydrogen-bond parameters (Å, °) for compound **1** at 293 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
293 K				
N3—H6C···Cl1^{ii}	0.96	2.59	3.423 (17)	146
N3—H6B···Cl5^{iii}	0.96	2.86	3.33 (2)	111
N3—H6B···Cl1^{iii}	0.96	2.88	3.743 (19)	150
N3—H6A···Cl1	0.96	2.49	3.423 (17)	164
N2—H2C···Cl2^{iv}	0.89	2.45	3.340 (10)	173
N2—H2B···Cl4^{v}	0.89	2.45	3.186 (13)	141
N2—H2A···Cl2^{vi}	0.89	2.62	3.340 (10)	138
N2—H2A···Cl1^{vi}	0.89	2.96	3.523 (10)	123
N2—H2A···Cl1^{vi}	0.89	2.96	3.523 (10)	123
N2—H2A···Cl2^{vi}	0.89	2.62	3.340 (10)	138
N2—H2B···Cl4^{v}	0.89	2.45	3.186 (13)	141
N2—H2C···Cl2^{iv}	0.89	2.45	3.340 (10)	173
N3—H6A···Cl1	0.96	2.49	3.423 (17)	164
N3—H6B···Cl1^{iii}	0.96	2.88	3.743 (19)	150
N3—H6B···Cl5^{iii}	0.96	2.86	3.33 (2)	111
N3—H6C···Cl1^{ii}	0.96	2.59	3.423 (17)	146

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

Table S9. Hydrogen-bond parameters (Å, °) for compound **2** at 170 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
170 K				
N2—H8C···Br4^{iii}	0.91	2.59	3.477 (8)	166
N2—H8B···Br6	0.91	2.68	3.484 (9)	148
N2—H8B···Br4^{iv}	0.91	3.02	3.567 (9)	120
N2—H8A···Br7	0.91	2.82	3.570 (9)	140
N2—H8A···Br6^{iii}	0.91	2.92	3.598 (8)	132
N1—H1C···Br2	0.91	2.43	3.316 (9)	165
N1—H1B···Br5^{v}	0.91	3.01	3.645 (8)	128

N1—H1B···Br5	0.91	2.60	3.323 (8)	137
N1—H1A···Br3^{v}	0.91	2.37	3.278 (8)	174
N3—H3C···Br5^{ii}	0.91	2.62	3.396 (8)	144
N3—H3C···Br2^{vi}	0.91	2.93	3.486 (8)	121
N3—H3B···Br6^{ii}	0.91	2.88	3.638 (8)	142
N3—H3B···Br3	0.91	2.73	3.325 (8)	124
N3—H3B···Br3^{vi}	0.91	2.63	3.513(8)	163

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

Table S10. Hydrogen-bond parameters (Å, °) for compound **2** at 293 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
293 K				
N1—H2F···Br2^{ii}	1.00	2.33	3.332 (16)	179
N1—H2E···Br2^{iii}	0.99	2.58	3.332 (16)	133
N1—H2D···Br4^{iv}	1.00	2.29	3.211 (18)	152
N3—H6C···Br1^{vi}	0.96	2.70	3.59 (2)	155
N3—H6B···Br1^{vii}	0.96	2.99	3.75 (2)	138
N3—H6B···Br1^{v}	0.96	2.99	3.75 (2)	138
N3—H6A···Br1	0.96	2.71	3.59 (2)	153
N2—H2C···Br2^{viii}	0.92	2.55	3.470 (15)	172
N2—H2B···Br4	0.94	2.50	3.319 (17)	146
N2—H2A···Br2^{ix}	0.91	2.75	3.470 (15)	136
N2—H2A···Br1^{ix}	0.91	3.12	3.682 (14)	121

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

Table S11. Hydrogen-bond parameters (Å, °) for compound **3** at 295 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
295 K				
N2—H2E···Cl5^{i}	0.89	2.35	3.218 (6)	164
N2—H2D···Cl4^{ii}	0.89	2.33	3.204 (6)	168
N2—H2C···Cl3^{ii}	0.89	2.68	3.281 (6)	126
N3—H3C···Cl3^{v}	0.89	2.60	3.380 (5)	147
N3—H3B···Cl6^{vi}	0.89	2.41	3.284 (5)	166
N3—H3A···Cl5^{v}	0.89	2.84	3.561 (5)	140
N3—H3A···Cl5	0.89	2.80	3.367 (6)	123
N3—H3A···Cl1^{v}	0.89	2.93	3.363 (5)	112
N1—H1E···Cl1^{vii}	0.89	2.52	3.378 (10)	161
N1—H1D···Cl6	0.89	2.84	3.444 (9)	126
N1—H1D···Cl2^{vii}	0.89	2.88	3.301 (9)	111

N1—H1C···Cl6^{vii}	0.89	2.94	3.680 (13)	142
N2—H2E···Cl5^{i}	0.89	2.35	3.218 (6)	164
N2—H2D···Cl4^{ii}	0.89	2.33	3.204 (6)	168
N2—H2C···Cl3^{ii}	0.89	2.68	3.281 (6)	126
N3—H3C···Cl3^{v}	0.89	2.60	3.380 (5)	147
N3—H3B···Cl6^{vi}	0.89	2.41	3.284 (5)	166
N3—H3A···Cl5^{v}	0.89	2.84	3.561 (5)	140
N3—H3A···Cl5	0.89	2.80	3.367 (6)	123
N3—H3A···Cl1^{v}	0.89	2.93	3.363 (5)	112
N1—H1E···Cl1^{vii}	0.89	2.52	3.378 (10)	161
N1—H1D···Cl6	0.89	2.84	3.444 (9)	126
N1—H1D···Cl2^{vii}	0.89	2.88	3.301 (9)	111
N1—H1C···Cl6^{vii}	0.89	2.94	3.680 (13)	142
N1—H1C···Cl6^{vii}	0.89	2.94	3.680 (13)	142
N1—H1D···Cl2^{vii}	0.89	2.88	3.301 (9)	111
N1—H1D···Cl6	0.89	2.84	3.444 (9)	126
N1—H1E···Cl1^{vii}	0.89	2.52	3.378 (10)	161
N3—H3A···Cl1^{v}	0.89	2.93	3.363 (5)	112
N3—H3A···Cl5	0.89	2.80	3.367 (6)	123
N3—H3A···Cl5^{v}	0.89	2.84	3.561 (5)	140
N3—H3B···Cl6^{vi}	0.89	2.41	3.284 (5)	166
N3—H3C···Cl3^{v}	0.89	2.60	3.380 (5)	147
N2—H2C···Cl3^{ii}	0.89	2.68	3.281 (6)	126
N2—H2D···Cl4^{ii}	0.89	2.33	3.204 (6)	168
N2—H2E···Cl5^{i}	0.89	2.35	3.218 (6)	164
N1—H1C···Cl6^{vii}	0.89	2.94	3.680 (13)	142
N1—H1D···Cl2^{vii}	0.89	2.88	3.301 (9)	111
N1—H1D···Cl6	0.89	2.84	3.444 (9)	126
N1—H1E···Cl1^{vii}	0.89	2.52	3.378 (10)	161
N3—H3A···Cl1^{v}	0.89	2.93	3.363 (5)	112
N3—H3A···Cl5	0.89	2.80	3.367 (6)	123
N3—H3A···Cl5^{v}	0.89	2.84	3.561 (5)	140
N3—H3B···Cl6^{vi}	0.89	2.41	3.284 (5)	166
N3—H3C···Cl3^{v}	0.89	2.60	3.380 (5)	147
N2—H2C···Cl3^{ii}	0.89	2.68	3.281 (6)	126
N2—H2D···Cl4^{ii}	0.89	2.33	3.204 (6)	168
N2—H2E···Cl5^{i}	0.89	2.35	3.218 (6)	164

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

Table S12. Hydrogen-bond parameters (Å, °) for compound **3** at 403 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
403 K				

N3—H3E···Cl3	0.90	2.30	2.93 (11)	126
N3—H3D···Cl9^{iii}	0.90	2.75	3.27 (7)	118
N3—H3D···Cl8^{iii}	0.90	2.32	2.99 (10)	131
N1—H1C···Cl9^{iv}	0.90	2.75	3.29 (2)	120
N1—H1B···Cl7^{ii}	0.90	2.77	3.47 (3)	136
N1—H1B···Cl7	0.90	2.96	3.47 (3)	118
N1—H1A···Cl9^{i}	0.90	2.41	3.29 (2)	166
N2—H2A···Cl7^{vii}	0.90	2.96	3.53 (3)	122
N3—H3E···Cl3	0.90	2.30	2.93 (11)	126
N1—H1C···Cl9^{iv}	0.90	2.75	3.29 (2)	120
N1—H1B···Cl7	0.90	2.96	3.47 (3)	118
N2—H2A···Cl7^{vii}	0.90	2.96	3.53 (3)	122
N1—H1A···Cl9^{i}	0.90	2.41	3.29 (2)	166
N1—H1B···Cl7	0.90	2.96	3.47 (3)	118
N1—H1B···Cl7^{ii}	0.90	2.77	3.47 (3)	136
N1—H1C···Cl9^{iv}	0.90	2.75	3.29 (2)	120
N3—H3D···Cl8^{iii}	0.90	2.32	2.99 (10)	131
N3—H3D···Cl9^{iii}	0.90	2.75	3.27 (7)	118
N3—H3E···Cl3	0.90	2.30	2.93 (11)	126

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

Table S13. Hydrogen-bond parameters (Å, °) for compound **4** at 289 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
289 K				
N1—H1C···Br2^{ii}	0.89	2.68	3.533 (10)	161
N1—H1B···Br5^{v}	0.89	2.79	3.505 (10)	138
N1—H1A···Br2^{v}	0.89	2.91	3.635 (12)	140
N3—H3C···Br4^{vi}	0.89	2.83	3.410 (9)	125
N3—H3B···Br3^{vi}	0.89	2.47	3.343 (8)	169
N3—H3A···Br1^{i}	0.89	2.50	3.353 (9)	162
N2—H2C···Br5	0.89	3.07	3.494 (7)	111
N2—H2C···Br1^{i}	0.89	2.93	3.488 (7)	123
N2—H2C···Br1	0.89	2.90	3.627 (7)	140
N2—H2B···Br2^{vii}	0.89	2.58	3.455 (7)	167
N2—H2A···Cl2	0.89	2.73	3.182 (7)	113
N2—H2A···Br4	0.89	2.71	3.491 (7)	147
N2—H2A···Br4	0.89	2.71	3.491 (7)	147
N2—H2A···Br4	0.89	2.71	3.491 (7)	147
N2—H2A···Cl2	0.89	2.73	3.182 (7)	113
N2—H2B···Br2^{vii}	0.89	2.58	3.455 (7)	167
N2—H2C···Br1	0.89	2.90	3.627 (7)	140

N2—H2C···Br1^{i}	0.89	2.93	3.488 (7)	123
N2—H2C···Br5	0.89	3.07	3.494 (7)	111
N3—H3A···Br1^{i}	0.89	2.50	3.353 (9)	162
N3—H3B···Br3^{vi}	0.89	2.47	3.343 (8)	169
N3—H3C···Br4^{vi}	0.89	2.83	3.410 (9)	125
N1—H1A···Br2^{v}	0.89	2.91	3.635 (12)	140
N1—H1B···Br5^{v}	0.89	2.79	3.505 (10)	138
N1—H1C···Br2^{ii}	0.89	2.68	3.533 (10)	161

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

Table S14. Hydrogen-bond parameters (Å, °) for compound **4** at 420 K.

D−H···A	**D-H**	**H···A**	**D···A**	**D−H···A**
420 K				
N3—H3A···Br9^{iii}	0.90	3.08	3.81 (3)	140
N3—H3A···Br8^{iv}	0.90	2.88	3.47 (4)	125
N1—H1C···Br9^{v}	0.90	3.10	3.564 (15)	114
N1—H1B···Br7^{ii}	0.90	2.92	3.581 (15)	132
N1—H1B···Br7	0.90	2.92	3.581 (15)	132
N1—H1A···Br9^{i}	0.90	2.71	3.564 (15)	160
N2—H2C···Br7^{ix}	0.90	3.14	3.795 (19)	132
N2—H2B···Br05^{ix}	0.90	2.57	3.28 (2)	137
N2—H2A···Br7^{x}	0.90	2.79	3.52 (2)	140

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