Supplementary Information

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Experimental Measurement Methods

X-ray Single Crystal Diffraction

Variable-temperature single-crystal X-ray diffraction information were collected by using Bruker APEX-II CCD with Mo Kα radiation (λ = 0.71073 Å). Compound **1** was collected at 300 K and 373 K, Compound **2** was collected at 273 K and 400 K, compound **3** was collected at 243 K and 403 K. Data processing was finished by APEX3. The crystal structure of compounds **1, 2** and **3** before and after phase transition were solved by direct method and refined by full-matrix least-squares methods based on F2 in the SHELXTL software package. All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The asymmetric unit and packing diagrams of compounds **1, 2** and **3** were drawn by DIAMOND software, other relevant crystallographic data and structure refinement of compounds **1, 2** and **3** are given in supporting information.

Powder X-ray Diffractions.

Powder X-ray diffraction (PXRD) data for compounds **1, 2** and **3** were measured on a D8 Advance03030502 X-ray diffractometer at room temperature. Diffraction patterns were collected in the 2θ range of 5−55° with a step size of 0.02°.

Thermal Measurements

DSC measurement was carried out by PerkinElmer diamond DSC instrument in a nitrogen atmosphere, 11 mg powder samples of compounds **1, 2** and **3** were weighed and placed in an aluminum crucible, the heating and cooling cycles were then carried out in the temperature range of 270 K to 370 K at a heating rate of 20 K min^{-1}. The temperature measurement range of compound **2** and compound **3** are 320 K to 400 K and 370 K to 420 K. Thermogravimetric analysis (TGA) was performed on a TA Q50 system in the temperature range of 300 K to 1023 K at a heating rate of 10 K min^{-1}.

Temperature-Dependent Dielectric Permittivity Measurements

Complex dielectric constants measurement in the heating and cooling cycles were performed on the Tonghui TH2828A instrument over the frequency range of 5 KHz to **1** MHz. The powder-pressed pellet of compounds **1, 2** and **3** pasted with carbon conducting glue was used in dielectric measurements.

Photoluminescence Spectrum Measurements

The solid-state excitation and emission spectra of compound **3** were measured on the Edinburgh FLS-920 fluorescence spectrometer. The absolute quantum efficiency is measured by the combined use of the Edinburgh FLS-920 fluorescence spectrometer and integrating sphere to obtain the photoluminescence quantum yield (PLQY).

Hirshfeld Surfaces and Intermolecular Interaction Analysis.

For compounds **1, 2** and **3**, the CrystalExplorer program was used to input the structure file in CIF format at 300/373 K, 273/400 K and 243/403 K, respectively, to calculate the Hirshfeld surface and 2D fingerprint[1]. The intensity of molecular interaction is expressed by mapping to the Hirshfeld surface using the corresponding red-blue-white scheme: where red, white, and blue represent contacts shorter than, equal to, and longer than the van der Waals distance, respectively. In the 2D fingerprint map, each point represents a pair (d_i, d_e), reflecting the distance between the inner (d_i) and outer (d_e)

nearest atoms of the Hirshfeld d_{norm} surface. The normalized contact distance d_{norm} is based on d_e, d_i and the van der Waals (vdW) radii of the two atoms external (r_e^{vdW}) and internal (r_i^{vdW}) to the surface:

$$d_{norm} = \frac{d_i - r^{vdW}}{r^{vdW}_i} + \frac{d_e - r}{r^{vdW}_e}$$

d_{norm} surface represents close intermolecular interactions.

For clear analysis and comparison, we focus on the selected cations with relatively stronger contacts in the respective structures.

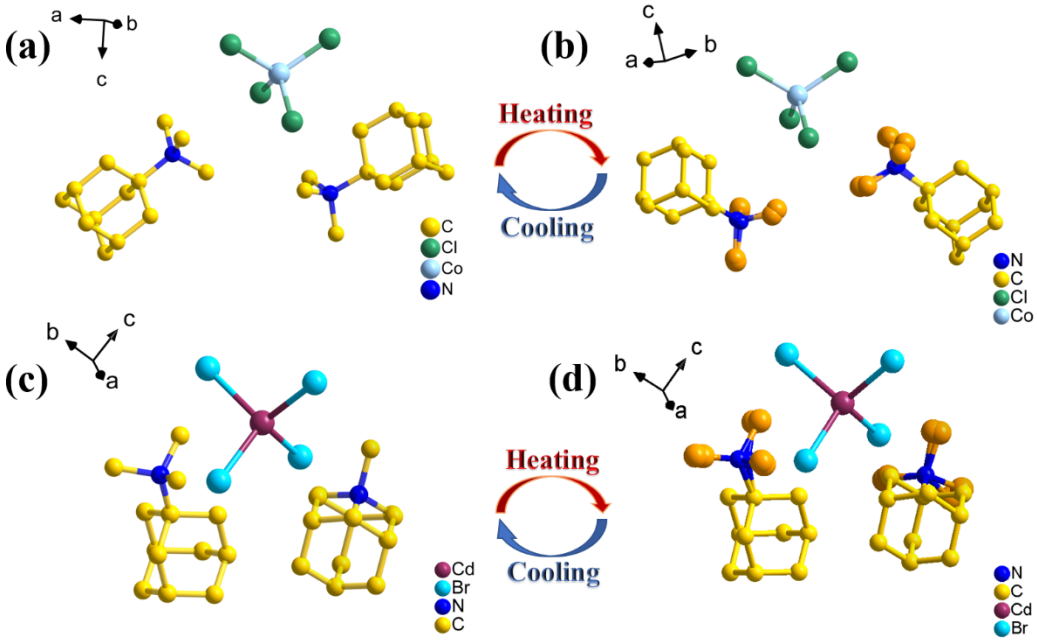

Figure S1. Structure of the minimum asymmetric unit at the low (a) and high temperature (b) for compound **1**. Structure of the minimum asymmetric unit at the low (c) and high temperature (d) for compound **2**.

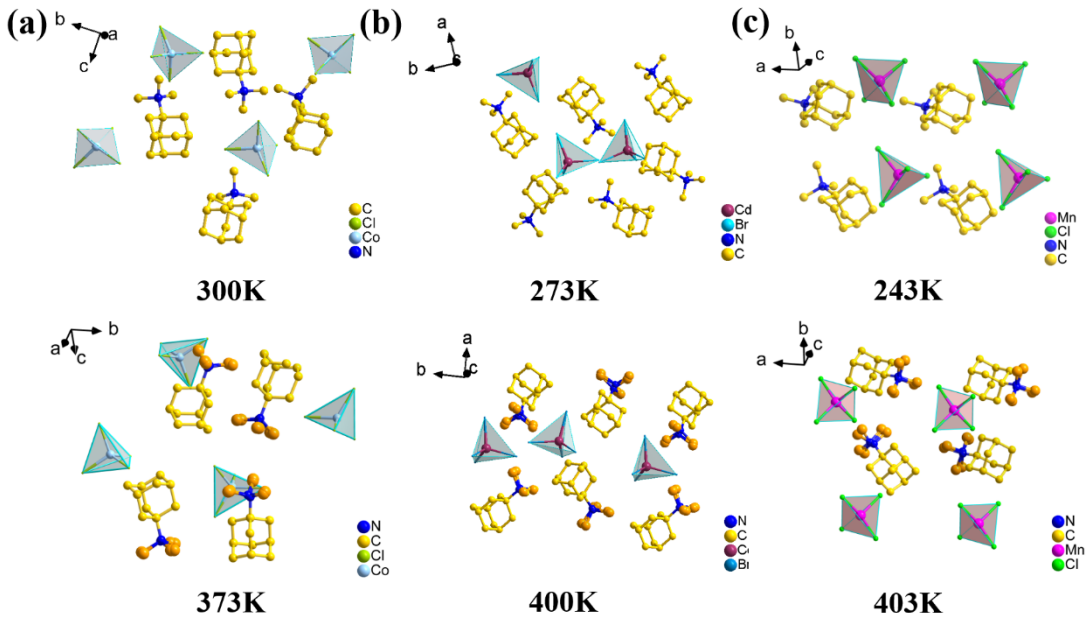

Figure S2. Packing views of compounds **1 (a)**, **2 (b)** and **3 (c)**.

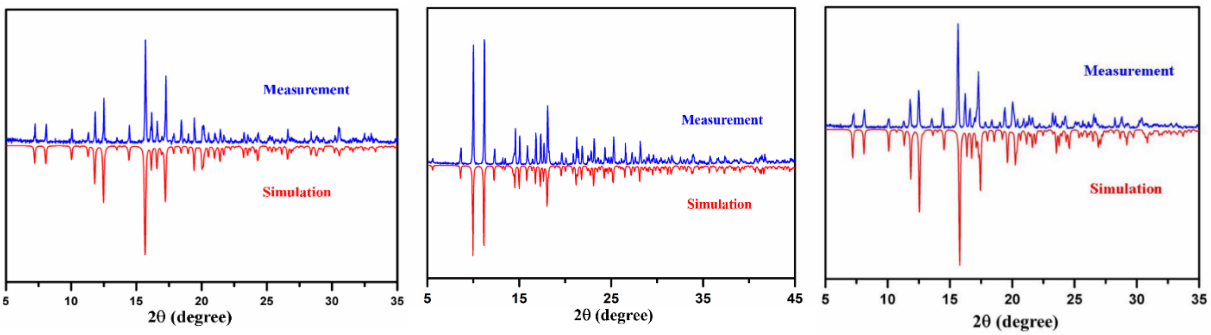

Figure S3. Measured and simulated powder X-ray diffraction patterns of compounds **1**(L), **2**（M）and **3** (R) at 298 K.

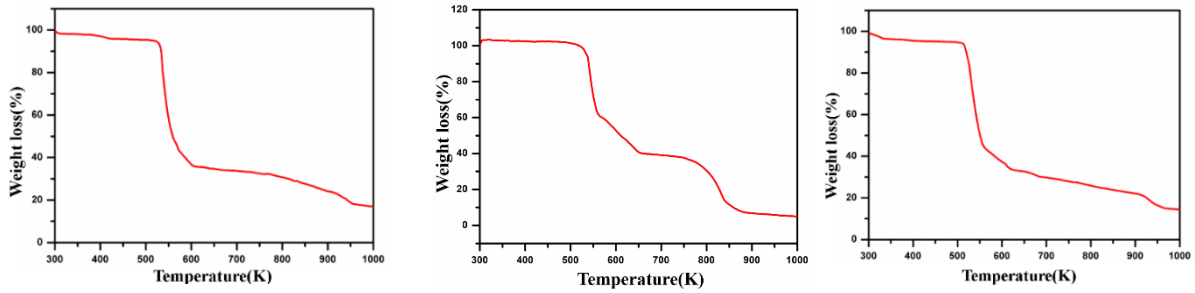

Figure S4. TGA curve of compounds **1** (L), **2** (M) and **3** (R) in the temperature range of 300 K-1000 K.

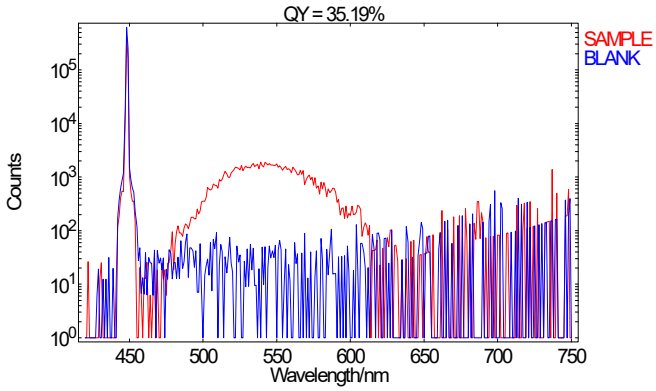

Figure S5. Fluorescence quantum yield of compound **3**.

Table S1. Crystal data and structure refinements for compound **1** at 300 K and 373 K

	LTP (300 K)	**HTP (373 K)**
Empirical formula	$C_{26}H_{48}Cl_4CoN_2$	$C_{26}H_{48}Cl_4CoN_2$
Formula weight	589.39	589.39
Space group	$P2_1/n$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic
a/ Å	8.957 (2)	8.998 (3)
b/ Å	21.945 (7)	22.109 (7)
c/ Å	14.812 (3)	14.924 (4)
β/°	92.853 (7)	92.965 (7)
Volume/ Å^3	2907.6 (13)	2964.69 (15)
Z	4	4
F(000)	1252	1252
GOF	1.029	1.027
$R_1[I>2\sigma(I)]$	0.0453	0.0488
$wR_2[I>2\sigma(I)]$	0.1181	0.1327

Table S2. Crystal data and structure refinements for compound **2** at 273 K and 400 K

	LTP (273 K)	**HTP (400 K)**
Empirical formula	$C_{26}H_{48}Br_4CdN_2$	$C_{26}H_{48}Br_4CdN_2$
Formula weight	820.70	820.70
Space group	$P2_1/c$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
a/ Å	16.129 (2)	16.265 (3)
b/ Å	13.449 (2)	13.5024 (19)
c/ Å	14.679 (2)	14.722 (2)
β/°	100.579 (3)	100.541 (4)
Volume/ Å^3	3130.0 (8)	3178.5 (9)
Z	4	4
F(000)	1624	1624
GOF	1.019	1.035
$R_1[I>2\sigma(I)]$	0.0713	0.064
$wR_2[I>2\sigma(I)]$	0.2006	0.1942

Table S3. Crystal data and structure refinements for compound **3** at 243 K and 403 K

	LTP (243 K)	**HTP (403 K)**
Empirical formula	$C_{26}H_{48}Cl_4MnN_2$	$C_{26}H_{48}Cl_4MnN_2$
Formula weight	585.40	585.40
Space group	$P2_1/n$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic
a/ Å	9.007 (3)	9.070(6)
b/ Å	21.927 (6)	22.174 (13)
c/ Å	14.922 (4)	15.094 (10)
β/°	92.838 (5)	93.162 (13)
Volume/ Å^3	2943.2 (14)	3031 (3)
Z	4	4
F(000)	1244	1244
GOF	1.029	1.051
$R_1[I>2\sigma(I)]$	0.0424	0.0836
$wR_2[I>2\sigma(I)]$	0.1038	0.2267

Table S4. Selected bond lengths [Å] and bond angles for compound **1** at 300 K.

bond lengths [Å]		bond angles [°]	
Cl1—Co1	2.2781 (12)	Cl4—Co1—Cl2	105.89 (5)
Cl2—Co1	2.2690 (11)	Cl4—Co1—Cl3	110.68 (5)
Cl3—Co1	2.2774 (11)	Cl2—Co1—Cl3	111.95 (4)
Cl4—Co1	2.2652 (11)	Cl4—Co1—Cl1	116.24 (4)
		Cl2—Co1—Cl1	107.23 (4)
		Cl3—Co1—Cl1	104.94 (4)

Table S5. Selected bond lengths [Å] and bond angles for compound **1** at 373 K.

bond lengths [Å]		bond angles [°]	
Cl1—Co1	2.2694 (13)	Cl3—Co1—Cl1	105.85 (6)
Cl2—Co1	2.2763 (13)	Cl3—Co1—Cl2	110.96 (7)
Cl3—Co1	2.2648 (15)	Cl1—Co1—Cl2	111.76 (5)
Cl4—Co1	2.2837 (14)	Cl3—Co1—Cl4	116.21 (6)
		Cl1—Co1—Cl4	107.20 (6)
		Cl2—Co1—Cl4	104.92 (5)

Table S6. Selected bond lengths [Å] and bond angles for compound **2** at 273 K.

bond lengths [Å]		bond angles [°]	
Cd1—Br4	2.5877 (7)	Br4—Cd1—Br3	115.20 (3)
Cd1—Br3	2.5972 (8)	Br4—Cd1—Br1	111.12 (2)
Cd1—Br1	2.6050 (7)	Br3—Cd1—Br1	107.90 (2)
Cd1—Br2	2.6181 (8)	Br4—Cd1—Br2	108.13 (2)
		Br3—Cd1—Br2	106.49 (3)
		Br1—Cd1—Br2	107.66 (2)

Table S7. Selected bond lengths [Å] and bond angles for compound **2** at 400 K.

bond lengths [Å]		bond angles [°]	
Cd1—Br4	2.5811 (7)	Br4—Cd1—Br1	115.63 (3)
Cd1—Br1	2.5914 (7)	Br4—Cd1—Br3	110.72 (2)
Cd1—Br3	2.5991 (8)	Br1—Cd1—Br3	107.41 (2)
Cd1—Br2	2.6111 (7)	Br4—Cd1—Br2	108.04 (2)
		Br1—Cd1—Br2	106.43 (2)
		Br3—Cd1—Br2	108.33 (2)

Table S8. Selected bond lengths [Å] and bond angles for compound **3** at 243 K.

bond lengths [Å]		bond angles [°]	
Mn1—Cl3	2.3551 (11)	Cl3—Mn1—Cl1	105.66 (4)
Mn1—Cl1	2.3639 (10)	Cl3—Mn1—Cl4	111.27 (4)
Mn1—Cl4	2.3679 (10)	Cl1—Mn1—Cl4	110.67 (4)
Mn1—Cl2	2.3701 (10)	Cl3—Mn1—Cl2	117.23 (4)
		Cl1—Mn1—Cl2	106.92 (4)
		Cl4—Mn1—Cl2	105.02 (4)

Table S9. Selected bond lengths [Å] and bond angles for compound **3** at 403 K.

bond lengths [Å]		bond angles [°]	
Mn1—Cl4	2.3457 (19)	Cl4—Mn1—Cl2	105.45 (7)
Mn1—Cl2	2.3519 (17)	Cl4—Mn1—Cl3	111.60 (7)
Mn1—Cl3	2.3546 (19)	Cl2—Mn1—Cl3	110.52 (6)
Mn1—Cl1	2.3708 (17)	Cl4—Mn1—Cl1	117.23 (7)
		Cl2—Mn1—Cl1	106.69 (7)
		Cl3—Mn1—Cl1	105.24 (6)

Table S10. Hydrogen-bond geometry (Å, °) for compound **1** at 300 K.

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21A···Cl1i	0.97	2.77	3.720 (4)	167
C16—H16C···Cl2	0.96	2.92	3.851 (4)	164
C16—H16A···Cl4ii	0.96	2.72	3.628 (4)	157
C15—H15A···Cl4ii	0.96	2.95	3.802 (4)	148
C14—H14C···Cl4ii	0.96	2.95	3.813 (4)	151
C14—H14A···Cl3	0.96	2.76	3.565 (4)	141
C12—H12A···Cl2	0.96	2.91	3.815 (5)	158
C11—H11B···Cl1iii	0.96	2.87	3.671 (5)	141
C10—H10B···Cl3iv	0.97	2.86	3.786 (4)	159
C5—H5B···Cl3iii	0.97	2.97	3.826 (4)	148
C1—H1A···Cl1iii	0.97	2.87	3.812 (4)	165
C1—H1A···Cl1iii	0.97	2.87	3.812 (4)	165
C5—H5B···Cl3iii	0.97	2.97	3.826 (4)	148
C10—H10B···Cl3iv	0.97	2.86	3.786 (4)	159
C11—H11B···Cl1iii	0.96	2.87	3.671 (5)	141
C12—H12A···Cl2	0.96	2.91	3.815 (5)	158
C14—H14A···Cl3	0.96	2.76	3.565 (4)	141
C14—H14C···Cl4ii	0.96	2.95	3.813 (4)	151
C15—H15A···Cl4ii	0.96	2.95	3.802 (4)	148
C16—H16A···Cl4ii	0.96	2.72	3.628 (4)	157
C16—H16C···Cl2	0.96	2.92	3.851 (4)	164
C21—H21A···Cl1i	0.97	2.77	3.720 (4)	167

Symmetry codes: (i) $x-1/2, -y+3/2, z+1/2$; (ii) $x+1/2, -y+3/2, z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+1, y, z$.

Table S11. Hydrogen-bond geometry (Å, °) for compound **1** at 373 K.

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16B···Cl4i	0.97	2.91	3.857 (5)	167
C15—H15A···Cl2ii	0.97	2.94	3.859 (5)	158
C3—H3A···Cl4iii	0.97	2.82	3.769 (5)	167
C13′—H13F···Cl3iv	0.96	2.94	3.81 (2)	151
C12′—H12E···Cl3iv	0.96	2.77	3.674 (19)	157
C11′—H11D···Cl2	0.96	2.77	3.47 (2)	130
C12—H12B···Cl3iv	0.96	2.65	3.59 (2)	165
C11—H11A···Cl2	0.96	2.88	3.686 (19)	142
C26′—H26E···Cl4	0.96	2.92	3.81 (2)	156
C14′—H14F···Cl1	0.96	3.06	3.94 (2)	152
C26—H26A···Cl4i	0.96	2.92	3.55 (2)	124
C14—H14C···Cl1	0.96	2.88	3.74 (2)	150
C16—H16B···Cl4i	0.97	2.91	3.857 (5)	167
C15—H15A···Cl2ii	0.97	2.94	3.859 (5)	158
C3—H3A···Cl4iii	0.97	2.82	3.769 (5)	167
C13′—H13F···Cl3iv	0.96	2.94	3.81 (2)	151
C12′—H12E···Cl3iv	0.96	2.77	3.674 (19)	157
C11′—H11D···Cl2	0.96	2.77	3.47 (2)	130
C12—H12B···Cl3iv	0.96	2.65	3.59 (2)	165
C11—H11C···Cl3iv	0.96	2.96	3.848 (16)	154
C11—H11A···Cl2	0.96	2.88	3.686 (19)	142
C26′—H26E···Cl4	0.96	2.92	3.81 (2)	156
C14′—H14F···Cl1	0.96	3.06	3.94 (2)	152
C26—H26A···Cl4i	0.96	2.92	3.55 (2)	124
C14—H14C···Cl1	0.96	2.88	3.74 (2)	150

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $x+1/2, -y+1/2, z-1/2$; (iv) $x-1/2, -y+1/2, z-1/2$.

Table S12. Hydrogen-bond geometry (Å, °) for compound **2** at 273 K.

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···Br2i	0.96	3.08	3.996 (9)	160
C13—H13C···Br3ii	0.96	3.04	3.877 (8)	146
C26—H26A···Br2	0.96	3.11	3.905 (7)	141
C10—H10A···Br4iii	0.97	3.01	3.885 (6)	151
C11—H11A···Br3iv	0.96	2.89	3.841 (6)	172
C25—H25A···Br2	0.96	3.00	3.876 (7)	153
C21—H21B···Br1v	0.97	3.08	4.011 (5)	161
C21—H21A···Br1ii	0.97	3.12	4.083 (5)	171
C21—H21A···Br1ii	0.97	3.12	4.083 (5)	171
C21—H21B···Br1v	0.97	3.08	4.011 (5)	161
C25—H25A···Br2	0.96	3.00	3.876 (7)	153
C11—H11A···Br3iv	0.96	2.89	3.841 (6)	172
C10—H10A···Br4iii	0.97	3.01	3.885 (6)	151
C26—H26A···Br2	0.96	3.11	3.905 (7)	141
C13—H13C···Br3ii	0.96	3.04	3.877 (8)	146
C12—H12A···Br2i	0.96	3.08	3.996 (9)	160
C21—H21A···Br1ii	0.97	3.12	4.083 (5)	171
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C26—H26A···Br2	0.96	3.11	3.905 (7)	141
C13—H13C···Br3ii	0.96	3.04	3.877 (8)	146
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C13—H13C···Br3ii	0.96	3.04	3.877 (8)	146
C12—H12A···Br2i	0.96	3.08	3.996 (9)	160

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

Table S13. Hydrogen-bond geometry (Å, °) for compound **2** at 400 K.

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10A···Br4i	0.97	3.07	3.959 (6)	152
C21—H21B···Br3ii	0.97	3.14	4.067 (5)	161
C16′—H16D···Br2ii	0.96	3.08	3.981 (10)	157
C15′—H15E···Br3	0.96	3.05	4.001 (10)	174
C15—H15B···Br2	0.96	3.10	3.932 (17)	146
C15—H15A···Br3	0.96	3.10	3.944 (19)	147
C14—H14C···Br2	0.96	3.09	3.840 (15)	136
C11′—H11F···Br1iii	0.96	2.89	3.835 (17)	170
C13—H13C···Br1iv	0.96	3.03	3.872 (12)	148
C12—H12B···Br2v	0.96	2.84	3.753 (10)	158
C11—H11B···Br1iii	0.96	2.97	3.915 (10)	170
C11—H11A···Br1iv	0.96	3.13	3.990 (13)	149
C10—H10A···Br4i	0.97	3.07	3.959 (6)	152
C21—H21B···Br3ii	0.97	3.14	4.067 (5)	161
C16′—H16D···Br2ii	0.96	3.08	3.981 (10)	157
C15′—H15E···Br3	0.96	3.05	4.001 (10)	174
C15—H15B···Br2	0.96	3.10	3.932 (17)	146
C15—H15A···Br3	0.96	3.10	3.944 (19)	147
C14—H14C···Br2	0.96	3.09	3.840 (15)	136
C11′—H11F···Br1iii	0.96	2.89	3.835 (17)	170
C13—H13C···Br1iv	0.96	3.03	3.872 (12)	148
C12—H12B···Br2v	0.96	2.84	3.753 (10)	158
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C11′—H11F···Br1iii	0.96	2.89	3.835 (17)	170
C14—H14C···Br2	0.96	3.09	3.840 (15)	136
C15—H15A···Br3	0.96	3.10	3.944 (19)	147
C15—H15B···Br2	0.96	3.10	3.932 (17)	146
C15′—H15E···Br3	0.96	3.05	4.001 (10)	174
C16′—H16D···Br2ii	0.96	3.08	3.981 (10)	157
C21—H21B···Br3ii	0.97	3.14	4.067 (5)	161
C10—H10A···Br4i	0.97	3.07	3.959 (6)	152

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

Table S14. Hydrogen-bond geometry (Å, °) for compound **3** at 243 K.

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15B···Cl2i	0.97	2.82	3.688 (4)	150
C14—H14C···Cl1	0.97	2.93	3.832 (4)	156
C14—H14B···Cl3ii	0.97	2.94	3.744 (4)	141
C12—H12C···Cl4	0.97	2.77	3.566 (4)	140
C12—H12A···Cl3ii	0.97	2.91	3.788 (4)	151
C17—H17B···Cl4i	0.98	2.93	3.802 (4)	149
C11—H11C···Cl3ii	0.97	2.94	3.805 (4)	149
C13—H13B···Cl1	0.97	2.90	3.847 (3)	166
C13—H13A···Cl3ii	0.97	2.72	3.622 (4)	154
C21—H21B···Cl4iii	0.98	2.85	3.783 (3)	158
C19—H19B···Cl2i	0.98	2.84	3.804 (3)	168
C8—H8B···Cl2iv	0.98	2.75	3.718 (3)	170
C15—H15B···Cl2i	0.97	2.82	3.688 (4)	150
C14—H14C···Cl1	0.97	2.93	3.832 (4)	156
C14—H14B···Cl3ii	0.97	2.94	3.744 (4)	141
C12—H12C···Cl4	0.97	2.77	3.566 (4)	140
C12—H12A···Cl3ii	0.97	2.91	3.788 (4)	151
C17—H17B···Cl4i	0.98	2.93	3.802 (4)	149
C11—H11C···Cl3ii	0.97	2.94	3.805 (4)	149
C13—H13B···Cl1	0.97	2.90	3.847 (3)	166
C13—H13A···Cl3ii	0.97	2.72	3.622 (4)	154
C21—H21B···Cl4iii	0.98	2.85	3.783 (3)	158
C19—H19B···Cl2i	0.98	2.84	3.804 (3)	168
C8—H8B···Cl2iv	0.98	2.75	3.718 (3)	170

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

Table S15. Hydrogen-bond geometry (Å, °) for compound **3** at 403 K.

D—H···A	D—H	H···A	D···A	D—H···A
C14′—H14D···Cl1i	0.96	2.84	3.750 (2)	159
C15′—H15F···Cl2	0.96	2.96	3.833 (3)	152
C16′—H16E···Cl2	0.96	2.81	3.715 (2)	158
C11—H11B···Cl4ii	0.96	2.51	3.453 (2)	167
C12—H12B···Cl3	0.96	2.93	3.721 (3)	141
C13—H13B···Cl2iii	0.96	2.97	3.802 (3)	146
C13—H13C···Cl4ii	0.96	2.99	3.820 (4)	146
C11′—H11D···Cl4ii	0.96	2.93	3.825 (2)	156
C12′—H12D···Cl4ii	0.96	2.89	3.799 (4)	158
C12′—H12F···Cl2	0.96	2.82	3.730 (5)	158
C8—H8B···Cl1iii	0.97	2.85	3.809 (6)	169
C20—H20A···Cl1i	0.97	2.92	3.885 (6)	171

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

Table S16. H_{inside}-$Cl_{outside}$ surface area, mean di and mean de of different amine in **1**、**2** and **3**.

Compound	**Temperature**	**H_{inside}-$Cl_{outside}$ surface area**		**Mean d_i**	**Mean d_e**
1	300 K	Cation 1	21.5%	1.5237	1.7259
		Cation2	21.3%	1.5457	1.7449
	373 K	Cation1	21.4%	1.5635	1.7543
		Cation2	22.0%	1.5677	1.7385
2	273 K	Cation1	22.6%	1.5560	1.8499
		Cation2	23.6%	1.5269	1.8035
	400 K	Cation1	22.9%	1.5969	1.8510
		Cation2	24.5%	1.5500	1.8119
3	243 K	Cation1	21.7%	1.5277	1.7388
		Cation2	21.8%	1.5414	1.7548
	403 K	Cation1	21.7%	1.5672	1.7603
		Cation2	21.9%	1.5727	1.7823

Reference

1.Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer17; University of Western Australia, 2017, http://hirshfeldsurface.net