Supporting Information

H/OH substitution achieving high-temperature multiferroicity in a Sn(IV)-based hybrid perovskite

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Supplementary Index

Experimental

Sample preparation.

Materials: $SnCl_4$•$5H_2O$ (≥98%, Shanghai Tian Scientific Co., Ltd.). $C_5H_{11}NO$•HCl (ShangHai Tian Scientific Co., Ltd.). HCl (36% ~ 38%, Jiangxi Xinguang Electronic Technology Co., Ltd.). All chemicals are commercially available and used directly without purification.

Synthesis of compound **3**: $C_5H_{11}NO$•HCl and $SnCl_4$•$5H_2O$ were weighed at stoichiometry 2:1, respectively. Using HCl (36% ~ 38%) solution as the solvent, it is slowly evaporated on a 333 K constant temperature heating table. After about seven days, a mixture containing precipitated crystals and mother liquor is obtained. Compounds **1** and **2** are synthesized in the same way as **3**.

General Measurements.

The Powder X-ray Diffraction (PXRD) was measured at a measurement angle of 5°–50° and a scan rate of 5°/min on the Rigaku D/MAX 2000 PC X-ray diffractometer. And the X-ray wavelength is 0.15406 nm. Samples of 14.8 mg of compound **1**, 14.2 mg of compound **2**, and 14.5 mg of compound **3** powder were weighed and placed in an aluminum crucible. Differential scanning calorimetry (DSC) was measured on a DSC 214 Polyma instrument under a nitrogen atmosphere with a heating/cooling rate of 15 K/min. The dielectric measurements of compound **3** were carried out on a Tonghui TH2828A impedance analyzer: the polycrystals of compound **3** were compacted into tight sheets, the thickness of the dielectric polycrystal was 0.472 mm, and both sides were coated with silver glue, the area of which was 2.073 mm^2, and tested in the temperature range of 385 K to 410 K, 500 Hz, 1 kHz, 5 kHz, 10 kHz, 100 kHz and 1 MHz of composite dielectric constant ($\varepsilon_r = \varepsilon' - i\varepsilon''$) changes with temperature. For second harmonic generation (SHG) measurements, an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used. The system is based on the theory of KURTZ about the SHG of crystalline powders. The size of the measured samples is about 200 mesh. 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. The *P*−*E* hysteresis loops were measured on a Radiant Precision Premier II. The instrument consists of Agilent 33500B (a waveform generator), Trek model 609E−6 (a high−voltage waveform amplifier), and Keithley 6517B (an electrometer).

X-ray diffraction experiments.

Variable-temperature X-ray diffraction analysis was carried out using a Rigaku synergy diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data collection, cell refinement, and data reduction were performed using CrysAlisPro (version 1.171.41.112a) XtaLAB Synergy-R online system. The structures were solved by the direct method and refined by the full-matrix method based on F^2 using the OLEX2 and SHELXTL (2018) software package. All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The organic cations were not modeled according to the chemical sense, because of the highly disordered form at the high-temperature phase. Detailed crystallographic data are recorded in **Tables S1–S8**. CCDC number: 2350423-2350425 contains supplemental crystallographic data for this article. These data are freely available from the Cambridge Crystallographic Data Centre.

Note 1: the procedure of entropy change (ΔS) and the ratio of the corresponding distinguishable geometric directions allowed by the high- and low-temperature phases (N) calculation for **3**.

Heating:

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{40.91\ J \cdot g^{-1} \times 535.72\ g \cdot mol^{-1}}{401\ K} = \frac{21916.3052\ J \cdot mol}{401\ K}$$

$$\cdot K^{-1}$$

$$\Delta S = R \ln N$$

$$N = \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{54.6541\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right) = 716.0450$$

Cooling:

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{39.92\, J \cdot g^{-1} \times 535.72\, g \cdot mol^{-1}}{394\, K} = \frac{21385.9424\, J \cdot mol}{394\, K}$$

$\cdot K^{-1}$

$$\Delta S = R \ln N$$

$$N = \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{54.2790\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right) = 684.4570$$

Supplemental Figures

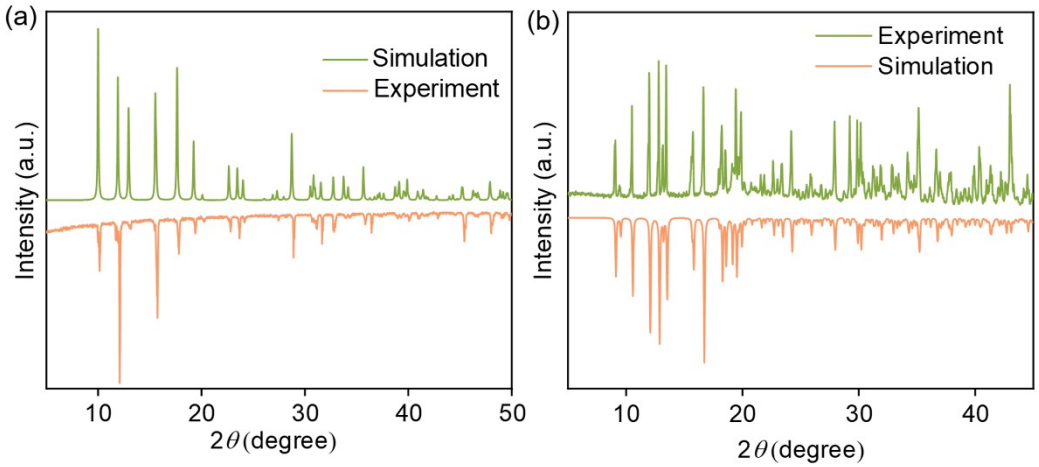

Figure S1. (a) PXRD patterns of compound **3** at 300 K and (b) PXRD patterns of compound **1** at 280.6 K.

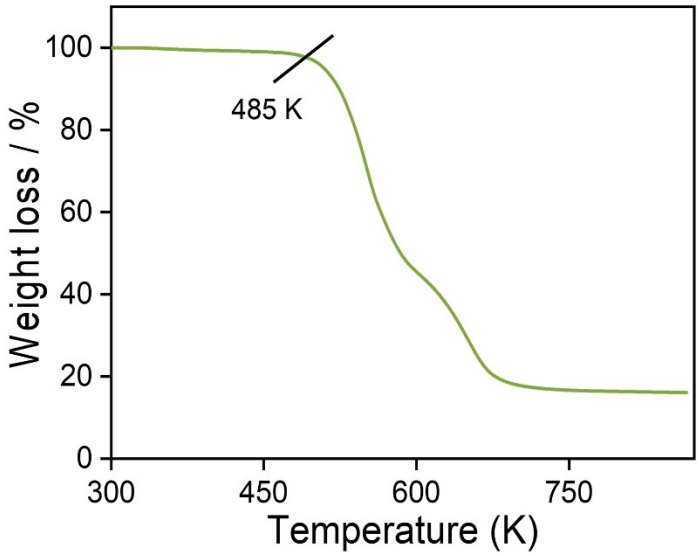

Figure S2. Thermogravimetric (TG) analysis curve of **3** around 300–800 K.

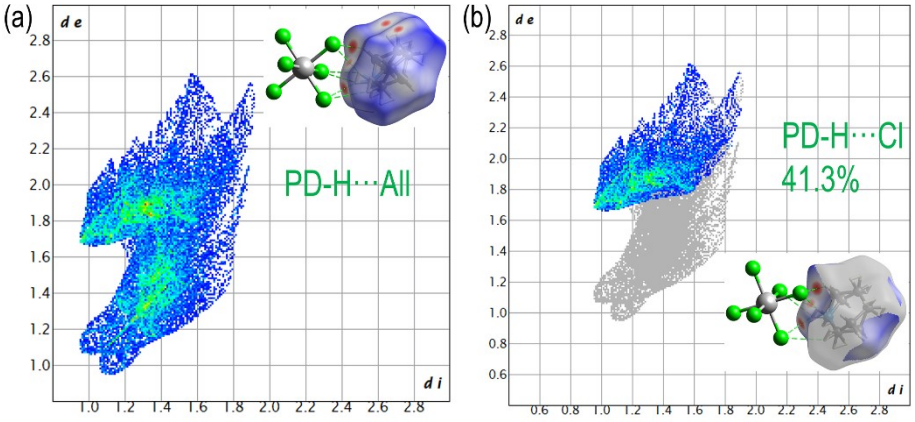

Figure S3. Hirshfeld surface analysis of hydrogen bonding interactions of the C_5H_9N molecular Cl^- and all elements substitution (in Figure PD is C_5H_9N).

(a)

```
Calculating, please wait...
Progress: [##################################################]   100.0 %     \
Volume of entire box:     971.741 Angstrom^3
Free volume:     260.077 Angstrom^3, corresponding to   26.76 % of whole space

Calculation took up time         0 s
```

(b)

```
Calculating, please wait...
Progress: [##################################################]   100.0 %     -
Volume of entire box:    2011.751 Angstrom^3
Free volume:     652.836 Angstrom^3, corresponding to   32.45 % of whole space

Calculation took up time         1 s
```

(c)

```
Calculating, please wait...
Progress: [##################################################]   100.0 %     -
Volume of entire box:    2011.389 Angstrom^3
Free volume:     652.184 Angstrom^3, corresponding to   32.42 % of whole space

Calculation took up time         0 s
```

Figure S4. (a) (b) (c) Multiwfn program calculations of the porosity of **1**, **2**, and **3**, respectively.

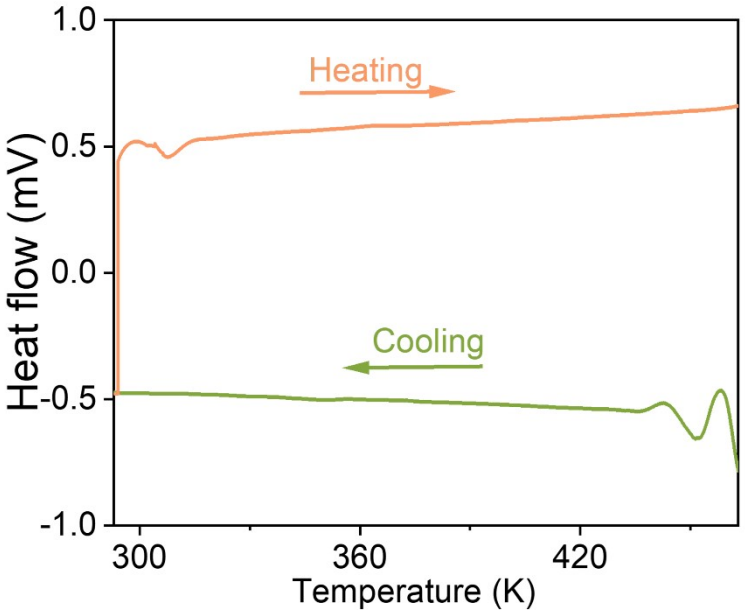

Figure S5. DSC curves of **1** at 295–435 K.

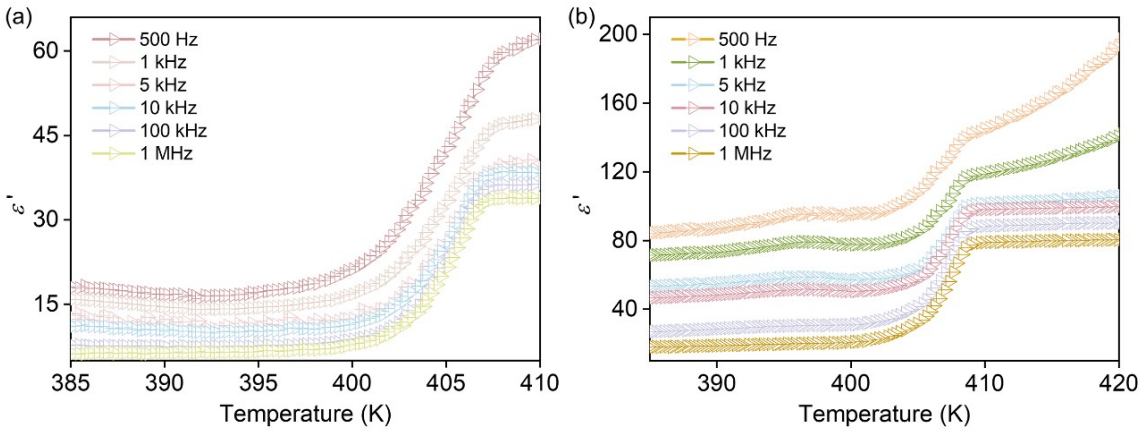

Figure S6. (a) The real part of the dielectric constant of crystal **3** along the *c*-axis electrode is measured at different frequencies during heating. (b) Measurement of ε' dielectric anomalies in powder samples of compound **3** heated at different frequencies.

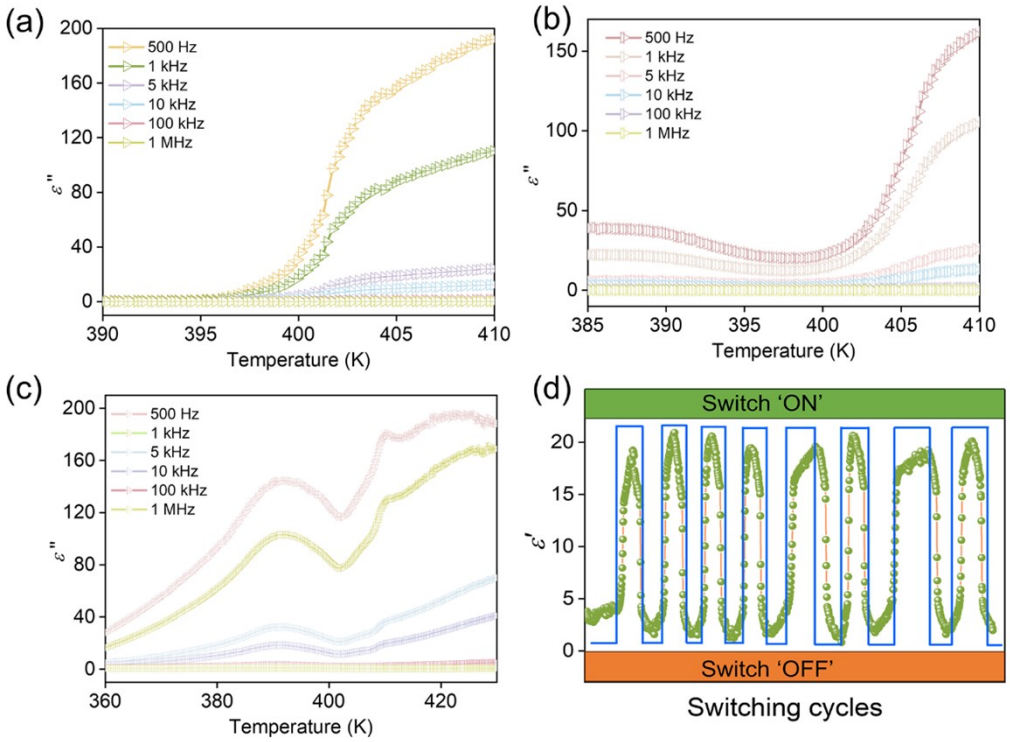

Figure S7. The imaginary part of the dielectric constant of crystal **3** along (a) the *b*-axis, (b) the *c*-axis and (c) the powder electrode is measured at different heating frequencies. (d) After 8 switching cycles at a frequency of 85 kHz, the value of the dielectric constant shows a sensitive switchable with no decrease.

Supplemental Tables

Table S1. Crystal Data and Structure Refinement Details for **3** at 298 K.

	1	**2**	**3**
T / *K*	280 K	300 K	300 K
Formula weight	480.01	1071.40	1071.40
Empirical formula	$C_{10}Cl_6N_2Sn_2H_{0.5}$	$C_{20}H_{48}Cl_{12}N_4O_4Sn_2$	$C_{20}H_{48}Cl_{12}N_4O_4Sn_2$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/m*	$P2_1$	$P2_1$
a / Å	17.6733(14)	9.2766(3)	9.2753(2)
b / Å	7.4068(6)	19.3762(7)	19.3722(5)
c / Å	7.4235(7)	11.2107(4)	11.2123(3)
α / °	90	90	90
β / °	90.307(8)	93.289(3)	93.265(3)
γ / °	90	90	90
V / Å^3	971.74(14)	2011.75(12)	2011.39(4)
Z	2	2	2
D_{calc} / g·cm^{-3}	1.641	1.769	1.769
μ / mm^{-1}	2.127	2.070	2.071
F(000)	453.0	1064.0	1064.0
2*θ range* / °	4.61−61.426	4.202−62.206	4.202−61.79
Reflns collected	6523	15146	18533
Independent reflns (R_{int})	1393(0.0705)	8465 (0.0278)	9053 (0.0307)
No. of parameters	56	383	383
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0604, 0.1675	0.0306, 0.0635	0.0323, 0.0704
R_1, wR_2 [all data]	0.1002, 0.1860	0.0372, 0.0657	0.0388, 0.0738
GOF	1.052	0.992	1.029
$\Delta\rho$[c] / e·Å^{-3}	1.63, −0.88	0.50, −0.53	0.50, −0.95
CCDC	2350423	2350425	2350424

[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 S2 Selected bond lengths [Å] and angles [°] for **1** at 280 K.

280 K			
Sn1−Cl6^{i}	2.4228 (14)	Cl6ii−Sn1−Cl6	91.76 (8)
Sn1−Cl6^{ii}	2.4228 (14)	Cl6iii−Sn1−Cl6	88.24 (8)
Sn1−Cl6^{iii}	2.4228 (14)	Cl6i−Sn1−Cl4i	90.07 (6)
Sn1−Cl6	2.4228 (14)	Cl6ii−Sn1−Cl4i	89.93 (6)
Sn1−Cl4^{i}	2.434 (2)	Cl6iii−Sn1−Cl4i	90.07 (6)
Sn1−Cl4	2.434 (2)	Cl6−Sn1−Cl4i	89.93 (6)
Cl6i−Sn1−Cl6^{ii}	88.24 (8)	Cl6ii−Sn1−Cl4	90.07 (6)
Cl6i−Sn1−Cl6^{iii}	91.76 (8)	Cl6iii−Sn1−Cl4	89.93 (6)
Cl6ii−Sn1−Cl6^{iii}	180.00 (5)	Cl6−Sn1−Cl4	90.07 (6)
Cl6i−Sn1−Cl6	180.0	Cl4i−Sn1−Cl4	180.0

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

Table S3 Selected bond lengths [Å] and angles [°] for **2** at 300 K.

300 K			
Sn1−Cl6	2.3829 (14)	Cl12−Sn1−Cl8	177.99 (6)
Sn1−Cl9	2.4128 (15)	Cl6−Sn1−Cl1	91.33 (5)
Sn1−Cl4	2.4217 (15)	Cl9−Sn1−Cl1	86.59 (6)
Sn1−Cl12	2.4294 (15)	Cl4−Sn1−Cl1	175.81 (5)
Sn1−Cl8	2.4320 (14)	Cl12−Sn1−Cl1	89.87 (5)
Sn1−Cl1	2.4880 (14)	Cl8−Sn1−Cl1	88.13 (5)
Sn2−Cl3	2.4105 (15)	Cl3−Sn2−Cl5	177.89 (8)
Sn2−Cl5	2.4169 (17)	Cl3−Sn2−Cl2	89.09 (7)
Sn2−Cl2	2.4229 (16)	Cl5−Sn2−Cl2	92.52 (8)

Sn2−Cl7	2.4269 (16)	Cl3−Sn2−Cl7	91.01 (6)
Sn2−Cl11	2.4342 (16)	Cl5−Sn2−Cl7	90.33 (6)
Sn2−Cl10	2.4358 (15)	Cl2−Sn2−Cl7	90.60 (7)
Cl6−Sn1−Cl9	177.69 (6)	Cl3−Sn2−Cl11	89.25 (7)
Cl6−Sn1−Cl4	92.81 (6)	Cl5−Sn2−Cl11	89.11 (8)
Cl9−Sn1−Cl4	89.29 (6)	Cl2−Sn2−Cl11	177.87 (8)
Cl6−Sn1−Cl12	90.43 (6)	Cl7−Sn2−Cl11	90.76 (7)
Cl9−Sn1−Cl12	90.56 (7)	Cl3−Sn2−Cl10	89.84 (6)
Cl4−Sn1−Cl12	89.47 (5)	Cl5−Sn2−Cl10	88.85 (6)
Cl6−Sn1−Cl8	89.74 (6)	Cl2−Sn2−Cl10	88.46 (6)
Cl9−Sn1−Cl8	89.20 (6)	Cl7−Sn2−Cl10	178.73 (7)
Cl4−Sn1−Cl8	92.52 (5)	Cl11−Sn2−Cl10	90.20 (6)

Symmetry codes:

Table S4 Selected bond lengths [Å] and angles [°] for **3** at 300 K.

300 K			
Sn1−Cl3	2.4867 (14)	Cl57−Sn1−Cl3	86.43 (6)
Sn1−Cl49	2.4198 (14)	Cl57−Sn1−Cl49	89.39 (7)
Sn1−Cl25	2.4338 (14)	Cl57−Sn1−Cl25	89.07 (6)
Sn1−Cl51	2.3864 (16)	Cl57−Sn1−Cl53	90.76 (7)
Sn1−Cl53	2.4282 (15)	Cl27−Sn2−Cl13	89.73 (6)
Sn1−Cl57	2.4138 (16)	Cl27−Sn2−Cl55	91.02 (6)
Sn2−Cl13	2.4375 (15)	Cl27−Sn2−Cl7	89.13 (7)
Sn2−Cl27	2.4095 (15)	Cl27−Sn2−Cl29	89.22 (7)
Sn2−Cl55	2.4293 (15)	Cl27−Sn2−Cl59	177.81 (8)

Sn2−Cl7	2.4285 (19)	Cl55−Sn2−Cl13	178.81 (7)
Sn2−Cl29	2.4360 (18)	Cl55−Sn2−Cl29	90.83 (7)
Sn2−Cl59	2.4166 (17)	Cl7−Sn2−Cl13	88.40 (6)
Cl49−Sn1−Cl3	175.77 (6)	Cl7−Sn2−Cl55	90.69 (7)
Cl49−Sn1−Cl25	92.49 (5)	Cl7−Sn2−Cl29	177.78 (8)
Cl49−Sn1−Cl53	89.54 (5)	Cl29−Sn2−Cl13	90.10 (6)
Cl25−Sn1−Cl3	88.09 (5)	Cl59−Sn2−Cl13	88.91 (6)
Cl51−Sn1−Cl3	91.44 (5)	Cl59−Sn2−Cl55	90.37 (6)
Cl51−Sn1−Cl49	92.74 (6)	Cl59−Sn2−Cl7	92.55 (9)
Cl51−Sn1−Cl25	89.68 (6)	Cl59−Sn2−Cl29	89.07 (9)

Symmetry codes: (i) [1]1-x, -1/2+y,2-z; (ii) 2+x,+y,1+z; (iii) [3]2-x,-1/2+y,1-z; (iv) [4]1-x,-1/2+y,1-z; [5]1+x,+y,+z; (v) [6]1+x,+y,-1+z; (vi) [7]-1+x,+y,+z; (vii)[8]-x,-1/2+y,2-z

Table S5 Selected bond lengths [Å] and angles [°] for **3** at 300 K.

300 K			
Sn1−Cl3	2.4867 (14)	Cl57−Sn1−Cl3	86.43 (6)
Sn1−Cl49	2.4198 (14)	Cl57−Sn1−Cl49	89.39 (7)
Sn1−Cl25	2.4338 (14)	Cl57−Sn1−Cl25	89.07 (6)
Sn1−Cl51	2.3864 (16)	Cl57−Sn1−Cl53	90.76 (7)
Sn1−Cl53	2.4282 (15)	Cl27−Sn2−Cl13	89.73 (6)
Sn1−Cl57	2.4138 (16)	Cl27−Sn2−Cl55	91.02 (6)
Sn2−Cl13	2.4375 (15)	Cl27−Sn2−Cl7	89.13 (7)
Sn2−Cl27	2.4095 (15)	Cl27−Sn2−Cl29	89.22 (7)
Sn2−Cl55	2.4293 (15)	Cl27−Sn2−Cl59	177.81 (8)
Sn2−Cl7	2.4285 (19)	Cl55−Sn2−Cl13	178.81 (7)

Sn2−Cl29	2.4360 (18)	Cl55−Sn2−Cl29	90.83 (7)
Sn2−Cl59	2.4166 (17)	Cl7−Sn2−Cl13	88.40 (6)
Cl49−Sn1−Cl3	175.77 (6)	Cl7−Sn2−Cl55	90.69 (7)
Cl49−Sn1−Cl25	92.49 (5)	Cl7−Sn2−Cl29	177.78 (8)
Cl49−Sn1−Cl53	89.54 (5)	Cl29−Sn2−Cl13	90.10 (6)
Cl25−Sn1−Cl3	88.09 (5)	Cl59−Sn2−Cl13	88.91 (6)
Cl51−Sn1−Cl3	91.44 (5)	Cl59−Sn2−Cl55	90.37 (6)
Cl51−Sn1−Cl49	92.74 (6)	Cl59−Sn2−Cl7	92.55 (9)
Cl51−Sn1−Cl25	89.68 (6)	Cl59−Sn2−Cl29	89.07 (9)

Symmetry codes: (i) [1]1-x, -1/2+y,2-z; (ii) [2]2+x,+y,1+z; (iii) [3]2-x,-1/2+y,1-z; (iv) [4]1-x,-1/2+y,1-z; [5]1+x,+y,+z; (v) [6]1+x,+y,-1+z; (vi) [7]-1+x,+y,+z; (vii)[8]-x,-1/2+y,2-z

Table S6. Bond lengths [Å] and bond angles [°] of the hydrogen bond at 280.6 K of **1**.

D−*H*···*A*	*D*−*H*	*H*···*A*	*D*···*A*	*D*−*H*···*A*
N2−H2B···Cl03	0.86	2.79	3.491 (13)	140
N2−H2B···Cl03^{i}	0.86	2.81	3.555 (12)	146

Symmetry code: (i) −x+1, y, −z+1.

Table S7. Bond lengths [Å] and bond angles [°] of the hydrogen bond at 280 K of **2**.

D−*H*···*A*	*D*−*H*	*H*···*A*	*D*···*A*	*D*−*H*···*A*
O1−H1···Cl10^{i}	0.82	2.60	3.354 (5)	153
C1−H1B···Cl1^{ii}	0.97	2.54	3.395 (5)	146
C1−H1A···Cl5	0.97	2.32	3.240 (6)	159
O2−H2···Cl1^{iii}	0.82	2.62	3.373 (5)	153
O3−H3···Cl12	0.82	2.65	3.292 (5)	136
N1−H1D···Cl10^{iv}	0.89	2.63	3.360 (5)	141
N1−H1C···O3	0.89	2.13	2.927 (7)	149
N4−H4C···Cl4	0.89	2.60	3.313 (6)	138
N4−H4B···O1	0.89	1.94	2.811 (7)	165
N2−H2A···Cl1^{iv}	0.89	2.69	3.395 (6)	137

N2−H2A···Cl8^{iv}	0.89	2.71	3.469 (6)	144
N2−H2B···Cl11^{i}	0.89	2.45	3.317 (6)	165

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

Table S8. Bond lengths [Å] and bond angles [°] of the hydrogen bond at 300 K of **3**.

D−*H*···*A*	*D*−*H*	*H*···*A*	*D*···*A*	*D*−*H*···*A*
O1−H1···Cl13^{i}	0.82	2.66	3.353 (5)	144
O1−H1···Cl29^{i}	0.82	2.82	3.433 (5)	133
N1−H1A···Cl55	0.89	3.03	3.573 (6)	121
N1−H1A···Cl59	0.89	2.39	3.244 (6)	160
N1−H1B···Cl3^{ii}	0.89	2.62	3.401 (6)	148
N1−H1B···Cl53^{ii}	0.89	2.97	3.499 (6)	120
N1−H1B···Cl57^{ii}	0.89	2.98	3.678 (6)	137
O4−H4···Cl3^{iii}	0.82	2.60	3.361 (6)	156
O2−H2···Cl55	0.82	2.94	3.531 (6)	131
O2−H2···O1	0.82	3.13	3.295 (8)	95
C1−H1C···Cl13^{iv}	0.97	2.57	3.359 (6)	139
C1−H1C···Cl27^{iv}	0.97	2.80	3.456 (6)	126
C1−H1C···Cl7^{iv}	0.97	2.91	3.680 (5)	137
C1−H1D···O4	0.97	2.63	2.925 (8)	98
C1−H1D···O3	0.97	2.05	2.922 (8)	149
O3−H3···Cl49	0.82	2.91	3.492 (5)	130
O3−H3···Cl53	0.82	2.69	3.300 (5)	132
N4−H4A···O4	0.89	2.68	2.946 (10)	99
N4−H4B···Cl57^{v}	0.89	3.12	3.470 (7)	106
N2−H2A···Cl3^{iv}	0.89	2.69	3.394 (6)	137
N2−H2A···Cl25^{iv}	0.89	2.70	3.466 (6)	145
N2−H2A···Cl57^{iv}	0.89	3.23	3.773 (7)	121
N2−H2B···Cl29^{i}	0.89	2.46	3.325 (7)	165
C4−H4C···Cl49	0.98	2.88	3.522 (6)	124
N3−H3C···O1	0.89	1.94	2.809 (8)	165
N3−H3C···O2	0.89	2.57	2.888 (9)	102

N3−H3D···Cl49	0.89	2.59	3.313 (6)	139
N3−H3D···Cl25	0.89	3.06	3.599 (6)	121

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