Electronic Supplementary Information (ESI)

A Hybrid Metal-Halide Antiperovskite Semiconductor Ferroelectric

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Methods

Crystal structure determination

Variable-temperature single-crystal diffraction data were collected on a Rigaku synergy diffractometer using Mo- K_α (λ= 0.71073 Å) radiation from a graphite monochromator. The crystal structures were resolved by direct method and then refined by the full-matrix least-square method based on F2 using the SHELXTL-2014 program. For the room temperature structures, non-hydrogen atoms were refined anisotropically and located in difference Fourier maps, however, the positions of hydrogen atoms were generated geometrically with Uiso = 1.2 Ueq (C and N). The B-site anion was first assigned to be the iodide ion. However, the thermal ellipsoid is larger than those of other iodide ions, and the donor-acceptor distances are shorter than the usual. Therefore, it was refined in the iodide-chloride disordered manner. For the intermediate temperature structure, the atoms corresponding to the organic ammonium can't be determined clearly from the Fourier difference map. They were modelled with geometries similar to those in the room temperature structure. For the high-temperature structure, the organic ammonium and the B-site iodide ion are disorder. Therefore, they were not modelled as the chemical sense. PXRD data was obtained on a Rigaku D/MAX 2000 PC X-ray diffractometer.

Thermal Measurements

Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch polyma differential scanning calorimeter under nitrogen at atmospheric pressure, with a heating/cooling rate of 10 K/min.

Absorption spectrum

The absorption spectrum was measured on a Perkin-Elmer Lambda 750S UV-VIS-NIR spectrometer. Ground crystals of 1 were used.

Dielectric and Ferroelectric Measurements

For dielectric and ferroelectric measurements, single-crystal pellets were prepared by grinding the crystals along the a-direction with sandpaper. The pellets have the thickness of around 0.3 mm and the area of around 4 mm2. Carbon conducting paste deposited on the surfaces was used as electrodes. A Tonghui TH2828A impedance analyzer was used to measure the dielectric constants. A Radiant Precision Premier II instrument was used to measure the P–E hysteresis loops.

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 applied. SHG performance of the sample was determined by comparison of the signal intensity with that of KDP (KH2PO4). The size of the measured samples is about 200 mesh.

Piezoresponse force microscopy.

Nanoscale polarization imaging and local switching spectroscopy were carried out using resonant-enhanced piezoresponse force microscopy (MFP-3D, Asylum Research). Conductive Pt/Ir-coated silicon probes (EFM-50, Nanoworld) were used for domain imaging and polarization switching studies. To verify the piezoresponse, we applied a 10 V AC driving voltage on the sample to measure the normal and shear responses, with the AC frequency set at the second resonant peak of a cantilever-sample system (340 kHz for normal response and 720 kHz for shear response) to enhance the sensitivity. The measurement was carried out on the thin grains, which were prepared as follows. Firstly, commercial ITO-coated glass substrate was sequentially ultrasonic cleaned in ethanol for 20 minutes. A drop of mother liquid of 1 in crystal growth was carefully spread on a freshly cleaned ITO-coated glass. The slow evaporation gave thin grains.

Theoretical calculation

The band structure and density of states were calculated using the DFT method within the CASTEP program (J. Phys.: Condens. Matter. 2002, 14, 2717; Int. J. Quantum Chem. 2000, 77, 895). The exchange and correlation effects were treated by GGA-PBE (Phys. Rev. Lett. 1996, 77, 3865). The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential (Phys. Rev. B. 1993, 47, 4174). The following valence–electron configurations were considered in the calculation: Pt-5s25p65d96s1, Cl-3s23p5, I-5s25p5, C-2s22p2, N-2s22p3 and H-1s1. In addition, a k-point sampling of 3 × 3 × 3 and cutoff energy of 570 eV were adopted.

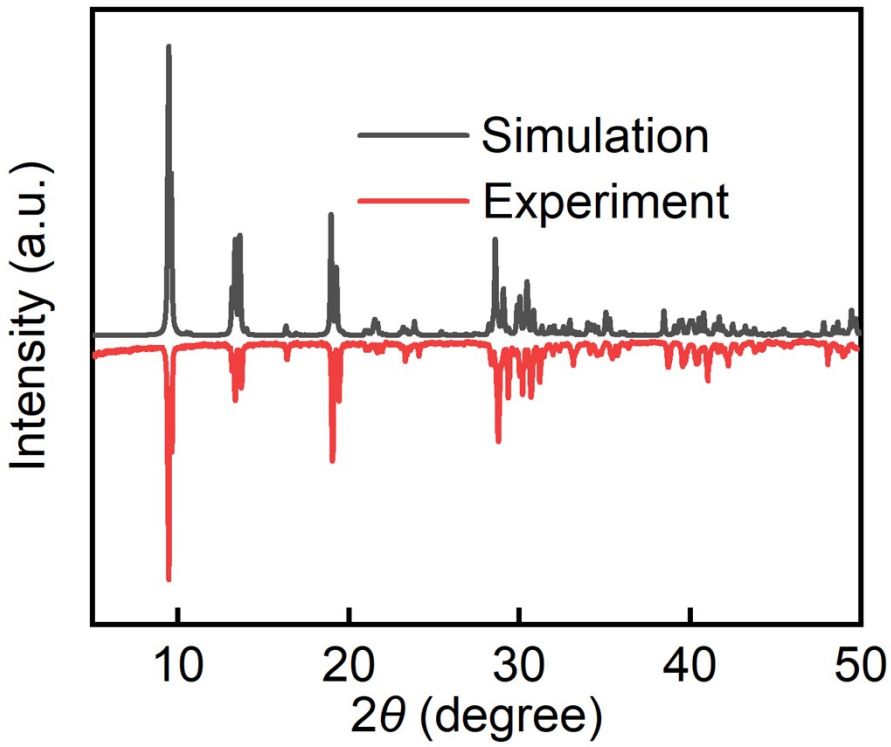

Fig. S1 PXRD patterns of **1**, verifying the purity of the bulk phase.

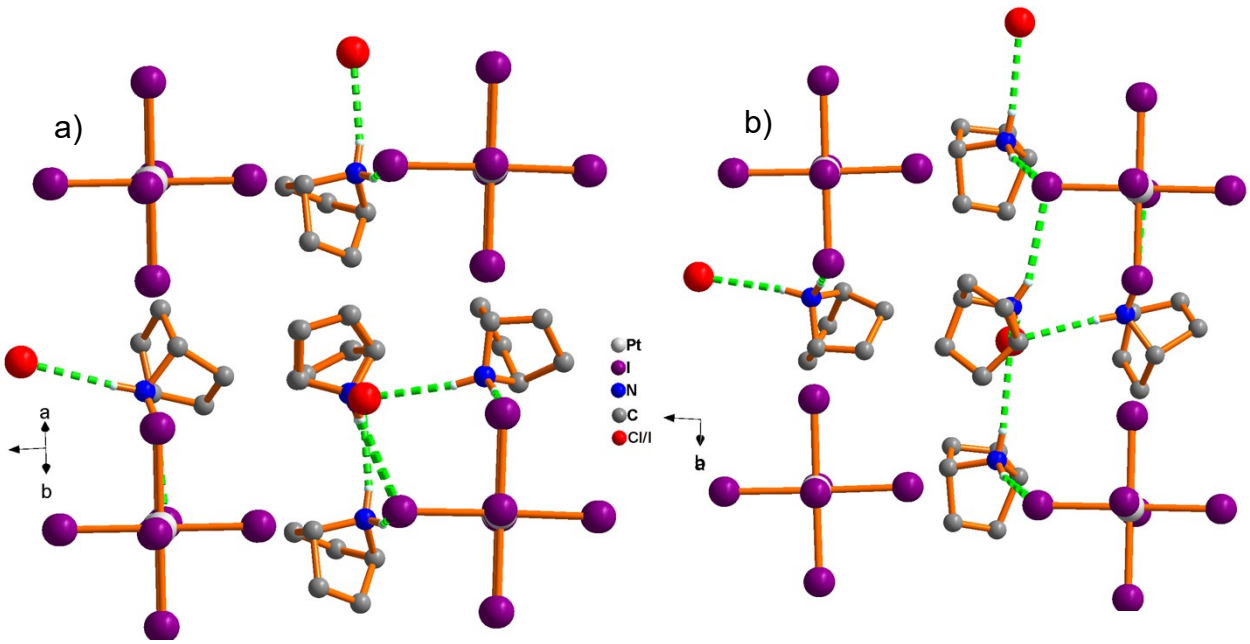

Fig. S2 (a) Hydrogen bond networks in **1**, viewed perpendicular to the hydrogen bond chains. (b) Hydrogen bond networks in **1**, viewed along the hydrogen bond chains.

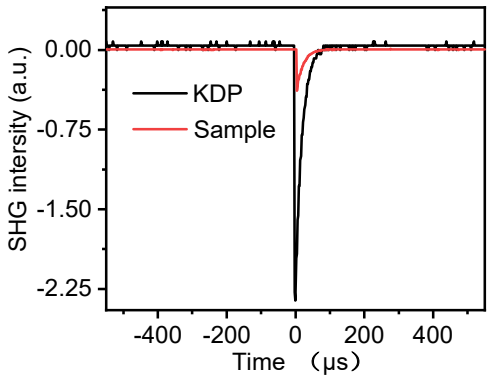

Fig. S3 Room temperature SHG intensity of **1**, compared with that of KH_2PO_4 (KDP).

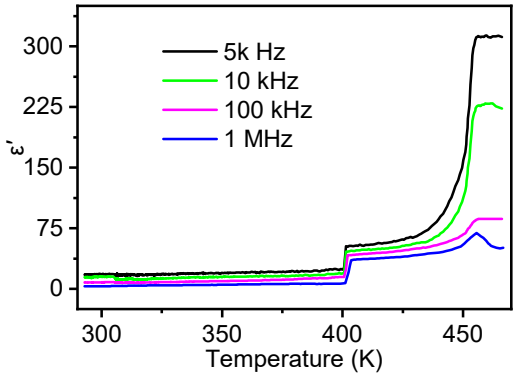

Fig. S4 Dielectric response of **1** at various frequencies in a heating process.

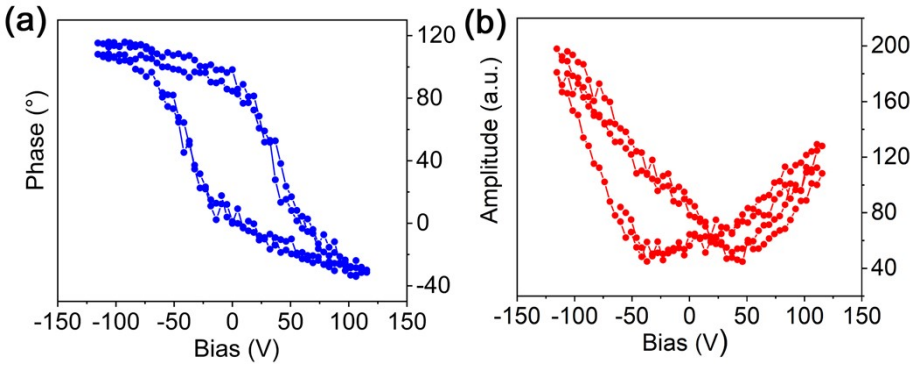

Fig. S5. (a,b) PFM amplitude and phase signals as functions of the tip voltage for a selected point.

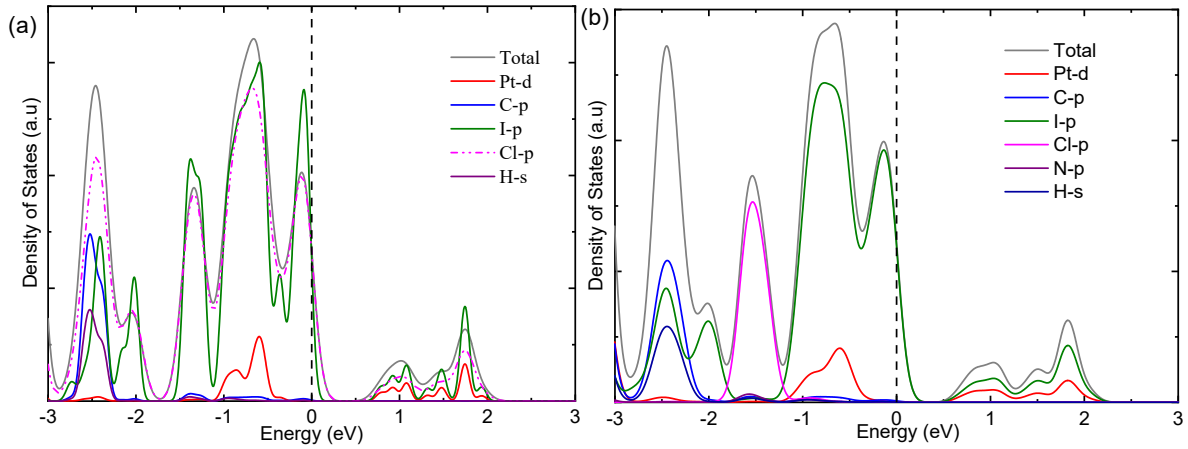

Fig. S6 Atom projected density of states in **1,** calculated with the model (a) that the B site is occupied by the I^- ion and Cl^- ion in a disordered manner and (b) that the B site is occupied only by the Cl^- ion.

Table S1. Effective radii (R_{eff}) of selected halogen and H_{abch}, MX_6^{2-} and Goldschmidt's tolerance factor (t) for predicted complexes.

Ion	R_{eff} (Å)	Ion	R_{eff} (Å)	Ion	R_{eff} (Å)
$PtCl_6^{2-}$	4.14	$SnCl_6^{2-}$	4.24	$TeCl_6^{2-}$	4.35
$PtBr_6^{2-}$	4.44	$SnBr_6^{2-}$	4.56	$TeBr_6^{2-}$	4.65
PtI_6^{2-}	4.88	SnI_6^{2-}	5.09	TeI_6^{2-}	5.14
Cl	1.81	Br	1.96	I	2.20
Habch	3.27				
Predicted compound:	t			Predicted	t
$(Habch)_3Cl(PtCl_6)$		1.03		$(Habch)_3Cl(TeCl_6)$	1.06
$(Habch)_3Br(PtBr_6)$		1.04		$(Habch)_3Br(TeBr_6)$	1.07
$(Habch)_3I(PtI_6)$		1.05		$(Habch)_3I(TeI_6)$	1.08
$(Habch)_3Cl(SnCl_6)$		1.05		$(Habch)_3Br(SnBr_6)$	1.06
$(Habch)_3I(SnI_6)$		1.08			