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# ESI

# Doping of Metal-free Molecular Perovskite with Hexamethylenetetramine to Create Non-centrosymmetric Defects

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#### 1. Sample preparation

Into 10 mL of an aqueous solution of dabco (0.232 g, 2.1 mmol), hmta (1.16 g, 8.3 mmol) and ammonium bromide (0.99 g, 10 mmol), aqueous solution of HBr (5 mL, 0.05 mol) were mixed. After 14 days, colorless block single crystals were obtained at the bottom of flask (yield 4.35 % for **d-Br**).



Figure S1-1. Schematic illustration of sample preparation.

Elemental Anal (%): calc C 19.21, H 4.81, N 11.96; found: C 19.392, H 4.773, N 11.370  $((C_6H_{14}N_2)_{0.9}(C_6H_{14}N_4)_{0.1}(NH_4)Br_3)$ 

FTIR (cm<sup>-1</sup>) : 3104 (br), 3007 (m), 2798 (w), 2584 (w), 1396.2 (s), 1317.1 (w), 1189.9 (m), 1051 (s), 889.02 (m), 854.31 (m), 804.17 (w)

### 2. Crystallography

Original cif files were obtained from previous reports and referred in table S2-1. In the **d-Br** of HTP, geometry of {(NH<sub>4</sub>)Br<sub>6</sub>} is regular octahedron with all Br-N(NH<sub>4</sub><sup>+</sup>)-Br angles  $\theta_{BrNBr}$  at 90°. Difference in octahedrons is appeared in  $\Sigma |\theta_{BrNBr}-90^{\circ}|$  that shows distortion from regular octahedron. Respective values of MTP **d-Br** and **h-Br** are 66.5° and 117.9°, showing distorted octahedron in the latter. Large distortion is originated from shift of central ammonium ions toward crystallographic  $\pm b-c$  direction. Orientation of two NH<sup>+</sup> moieties of hmtaH<sub>2</sub><sup>2+</sup> is interacted with the shift of ammonium and causing spontaneous dipole moment in **h-Br**. These mismatches of octahedrons are affective to fluctuated disorder around hmtaH<sub>2</sub><sup>2+</sup>.

Compounds	h-Br	d-Br(MTP)	d-Br(HTP)	
Temperature / K	253 K	293 K	355 K	
θ <sub>BrNBr</sub> / degree	79.47, 68.20, 79.47,	83.05, 87.19, 94.23,		
	89.78, 77.03, 77.03,	86.30, 97.15, 102.11,	00	
	96.67, 96.67, 89.21,	86.27, 83.05, 85.33,	90	
	112.81, 95.97, 95.97	97.19, 94.23, 87.22		
Max/Min	112.81/68.20	102.11/83.05	90/90	
Σ  <i>θ</i> <sub>BrNBr</sub> -90	117.9	66.5	90	
Volume of octahedrons	E1 G	<b>FA A</b>	51.6	
(V <sub>0</sub> ) / Å <sup>3</sup>	01.0	51.4		
Volume of unit cell per	200.9	200.2	309.6	
molecule ( <i>V/Z</i> ) / ų	509.0	300.2		
Volume of A-cation	250.2	256.9	259.0	
$= V/Z - V_{\rm O}$	200.2	200.8	238.0	
References	13	12	12	

Table S2-1. Br-N-Br angles  $\theta_{BrNBr}$  in the octahedrons of **h-Br** and **d-Br** (data from reported cif files). Reference numbers are corresponded to those in main text.

(a)

3 430

3.423

3.358

3.423





(C)



Figure S2-1. Interatomic distances between N (NH<sub>4</sub><sup>+</sup>) and Br<sup>-</sup> of (a) **d-Br** (MTP), (b) **d-Br** (HTP) and (c) **h-Br** (data from reported cif files; references 12 and 13 in the main text).

HB

3.383

Single crystal XRD analysis at LTP of **d-Br** was performed at 100 K. Dabco molecule is statically disordered with employing different orientations. By comparing to structure solved at MTP, phase transition was understood by order-disorder type transition. At MTP, dabco skeleton is dynamically disordered with torsional motion. Differences in space group are not intrinsic transition. Chirality is originated from orientation of dabco molecule in the perovskite lattice. This is not considered to be transited between MTP and LTP.

#### LTP of d-Br; CCDC-1979316

 $C_6H_{14}Br_3N_3$ , M = 365.92, trigonal, a = 9.6026(5), c = 23.3261(12) Å, V = 1862.7(2) Å<sup>3</sup>, T = 100 K, space group  $P3_221$  (no.154), Z = 6, 16096 reflections measured, 3613 unique ( $R_{int} = 0.0842$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1282 (all data). Statically disordered C5 and C6 are difficult to be solved with anisotropic thermal ellipsoid. This would be originated from existence of other possible static disorder. Protons on N atoms of ammonium were not assigned. Detail of structure at LTP will be investigated in depth.



Figure S2-2 Ortep view of structure at 100 K of d-Br.

#### 3. Powder XRD

Measurements were performed using a Rigaku Mini Flex 600 attached with temperature control chamber.



Figure S3-1. Simulated powder XRD patterns of **d-Br** (MTP and HTP) and **h-Br** with experimental results of **(d, h)-Br** at 293 and 355 K.

Table S3-1. Comparison of crystallographic data. Values of (d, h)-Br were estimated from powder XRE
results given by Cubic phase.*data was caluculated from powder XRD pattern reported by us (reference
13 in main text).

Compounds	d-Br	(d, h)-Br	h-Br	
Lattice	Cu	Cubic		nombic
Temperature /K	35	55	253	358*
a / Å	6.765	6.785	13.4615	13.801
b/Å			6.7669	6.793
c / Å			6.8027	6.857
V / Å <sup>3</sup>	309.6	312.5	619.68	642.8
V/Z / Å <sup>3</sup>	309.6	312.5	309.8	321.4

# 4. DSC

DSC measurements were performed using a RIGAKU Thermo plus evo II.



Figure S4-1. DSC trace of d-Br and (d, h)-Br. Shoulders around 200 K for cooling process are originated from changes of *dT/dt*.

	d-Br	(d,h)-Br
<i>Т</i> <sub>с1</sub> / К	180	180
$\Delta H_1$ / kJmol <sup>-1</sup>	-2.0	-1.5
<i>T</i> <sub>c2</sub> / K	330	unclear
$\Delta H_2$ / kJmol <sup>-1</sup>	-3.4	-2.5

Table S4-1. Summary of thermal analysis by DSC.

#### 5. Complex dielectric constant measurement

Dielectric permittivity measurements were performed by ac two-probe measurements using pellets. Gold paste was used for electrodes and electrical contacts were made using gold wires. Temperaturedependent dielectric permittivity was measured using an Agilent E4980A Precision LCR meter in an air atmosphere. The typical applied ac voltage was 1 V, and the frequency range was 100 Hz–1 MHz. Temperature dependence were measured under vacuum using a commercially available cryostat with a temperature control system over the temperature range 10-400 K.



Figure S5-1. Real part and imaginal part of dielectric complex of (d, h)-Br at 10-300 K.



Figure S5-2. Real part and imaginal part of dielectric complex of (d, h)-Br above 300 K (300 to 400 K).



Figure S5-3. Tangent delta of dielectric complex of (d, h)-Br above 300 K.



Figure S5-4. Arrhenius plots for relaxation  $r_1$  and  $r_2$ .

Table S5-1. Summary of activation energies and blocking temperature ( $T_b$ ) estimated at 0.1 Hz.

	r <sub>1a</sub>	r <sub>1b</sub>	<b>r</b> <sub>2</sub>
E <sub>a</sub> / eV	0.72	0.37	0.55
<i>T</i> <sub>b</sub> (0. 1 Hz) / K	163	133	186



Figure S5-5. Real and imaginal part of dielectric complex of **(d, h)-Br** for cycle measurements at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

(300 K→400 K→300 K)

# 6. NMR

Solid state CP-MAS-<sup>13</sup>C-NMR (150.872 MHz) measurements were performed using a NMR Varian600 at spinning speed at 20 kHz.





Figure S6-1. <sup>13</sup>C-NMR of **d-Br** (blue), **h-Br** (pink) and (**d**, **h**)-**Br** at 300 K (gray) and 343 K (black).