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Supporting Information

Investigations of organic-inorganic hybrids based on homopiperidinium cation with haloantimonates(III) and halobismuthates(III). Crystal structures, reversible phase transitions, semiconducting and molecular dynamic properties.

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TABLE OF CONTENS:

- 1. X-ray characterization;
- 2. Thermal properties;
- 3. Electric properties;
- 4. ¹H NMR solid state;
- 5. Second harmonic generation (SHG).

<u>PART 1</u>



Fig. S1. X-ray diffraction pattern of HSC, HSB, HBC and HBB at 298 K and calculated from crystal structures.



Fig. S2. The model of asymmetric unit of the **HSB** crystal structure at a) 310 and b) 150 K. The transparent of the yellow, light blue or brown atoms shown disordered.

Table S1. Hydrogen-bond geometry [Å, °] for **HSC** at a) 280 K and b) 150 K.

a)

D—H…A	D—H	H…A	D···A	D—H…A	
N1A-H1A1…Cl5	0.89	2.35	3.236(11)	173	
N1A—H1A2…Cl3 ⁱ	0.89	2.49	3.259(10)	145	
N1B—H1B1…Cl4	0.89	2.46	3.291(10)	155	
N1B—H1B2…Cl2 ⁱ	0.89	2.80	3.637(17)	157	

b)

D—H…A	D—H	H…A	D…A	D—H…A	
N1A—H1A1…Cl5	0.91	2.29	3.192(5)	172	
N1A—H1A2…Cl3 ⁱ	0.91	2.45	3.230(5)	145	
N1B—H1B1…Cl4	0.91	2.42	3.251(5)	152	
N1B—H1B2…Cl2 ⁱ	0.91	2.55	3.442(6)	168	

Symmetry code: (i) x+1, y, z.

a)

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb-Cl1	2.387(3)	Cl1—Sb—Cl2	88.51(10)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb—Cl2	2.528(2)	Cl1—Sb—Cl3	90.53(11)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb—Cl3	2.592(3)	Cl2—Sb—Cl3	88.16(10)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb—Cl4	2.683(3)	Cl1—Sb—Cl4	87.92(10)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sb—Cl5	2.781(3)	Cl2—Sb—Cl4	88.44(10)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sb—Cl4 ⁱ	3.360(3)	Cl3—Sb—Cl4	176.30(10)
$\begin{array}{c ccccc} N1A-C2A & 1.505(14) & Cl2-Sb-Cl5 & 172.55(9) \\ C2A-C3A & 1.486(16) & Cl3-Sb-Cl5 & 92.32(9) \\ C3A-C4A & 1.47(2) & Cl4-Sb-Cl5 & 90.86(9) \\ C4A-C5A & 1.45(2) & Cl1-Sb-Cl4^i & 166.75(9) \\ C5A-C6A & 1.43(3) & Cl2-Sb-Cl4^i & 80.63(8) \\ C5A-C61A & 1.37(5) & Cl3-Sb-Cl4^i & 96.66(10) \\ C6A-C7A & 1.48(3) & Cl4-Sb-Cl4^i & 84.23(4) \\ C61A-C7A & 1.49(5) & Cl5-Sb-Cl4^i & 106.68(8) \\ N1A-C7A & 1.488(15) \\ \hline \\ N1B-C2B & 1.420(15) \\ C2B-C3B & 1.476(18) \\ C3B-C4B & 1.49(2) \\ C4B-C5B & 1.511(18) \\ C5B-C6B & 1.497(18) \\ C6B-C7B & 1.485(18) \\ N1B-C7B & 1.469(18) \\ \hline \end{array}$			Cl1—Sb—Cl5	84.05(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1A—C2A	1.505(14)	Cl2—Sb—Cl5	172.55(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2A—C3A	1.486(16)	Cl3—Sb—Cl5	92.32(9)
$\begin{array}{cccccccc} C4A-C5A & 1.45(2) & Cl1-Sb-Cl4^i & 166.75(9) \\ C5A-C6A & 1.43(3) & Cl2-Sb-Cl4^i & 80.63(8) \\ C5A-C61A & 1.37(5) & Cl3-Sb-Cl4^i & 96.66(10) \\ C6A-C7A & 1.48(3) & Cl4-Sb-Cl4^i & 84.23(4) \\ C61A-C7A & 1.49(5) & Cl5-Sb-Cl4^i & 106.68(8) \\ N1A-C7A & 1.488(15) \\ \end{array}$	C3A—C4A	1.47(2)	Cl4—Sb—Cl5	90.86(9)
$\begin{array}{ccccccc} C5A-C6A & 1.43(3) & Cl2-Sb-Cl4^i & 80.63(8) \\ C5A-C61A & 1.37(5) & Cl3-Sb-Cl4^i & 96.66(10) \\ C6A-C7A & 1.48(3) & Cl4-Sb-Cl4^i & 84.23(4) \\ C61A-C7A & 1.49(5) & Cl5-Sb-Cl4^i & 106.68(8) \\ N1A-C7A & 1.488(15) & & & & & & \\ \end{array}$	C4A—C5A	1.45(2)	Cl1—Sb—Cl4 ⁱ	166.75(9)
C5A—C61A 1.37(5) Cl3—Sb—Cl4 ⁱ 96.66(10) C6A—C7A 1.48(3) Cl4—Sb—Cl4 ⁱ 84.23(4) C61A—C7A 1.49(5) Cl5—Sb—Cl4 ⁱ 106.68(8) N1A—C7A 1.488(15) 106.68(8) 106.68(8) N1B—C2B 1.420(15) 106.68(8) 106.68(8) C2B—C3B 1.476(18) 23B—C4B 1.49(2) C4B—C5B 1.511(18) C5B—C6B 1.497(18) C6B—C7B 1.485(18) N1B—C7B 1.469(18)	C5A—C6A	1.43(3)	Cl2—Sb—Cl4 ⁱ	80.63(8)
C6AC7A 1.48(3) Cl4-SbCl4 ⁱ 84.23(4) C61AC7A 1.49(5) Cl5SbCl4 ⁱ 106.68(8) N1AC7A 1.488(15) 106.68(8) N1BC2B 1.420(15) 106.68(8) C2BC3B 1.476(18) 106.68(8) C3BC4B 1.49(2) 106.68(8) C4BC5B 1.511(18) 106.68(8) C5BC6B 1.497(18) 106.68(8) C6BC7B 1.485(18) 106.68(8) N1BC7B 1.469(18) 106.68(8)	C5A—C61A	1.37(5)	CI3—Sb—CI4 ⁱ	96.66(10)
C61AC7A 1.49(5) Cl5SbCl4 ⁱ 106.68(8) N1AC7A 1.488(15) 106.68(8) N1BC2B 1.420(15) 106.68(8) C2BC3B 1.476(18) 106.68(8) C3BC4B 1.49(2) 106.68(8) C4BC5B 1.511(18) 106.68(8) C5BC6B 1.497(18) 106.68(8) C6BC7B 1.485(18) 1.496(18)	C6A—C7A	1.48(3)	Cl4—Sb—Cl4 ⁱ	84.23(4)
N1AC7A 1.488(15) N1BC2B 1.420(15) C2BC3B 1.476(18) C3BC4B 1.49(2) C4BC5B 1.511(18) C5BC6B 1.497(18) C6BC7B 1.485(18) N1BC7B 1.469(18)	C61A—C7A	1.49(5)	CI5—Sb—CI4 ⁱ	106.68(8)
N1B-C2B 1.420(15) C2B-C3B 1.476(18) C3B-C4B 1.49(2) C4B-C5B 1.511(18) C5B-C6B 1.497(18) C6B-C7B 1.485(18) N1B-C7B 1.469(18)	N1A—C7A	1.488(15)		
N1BC2B 1.420(15) C2BC3B 1.476(18) C3BC4B 1.49(2) C4BC5B 1.511(18) C5BC6B 1.497(18) C6BC7B 1.485(18) N1BC7B 1.469(18)				
C2B-C3B 1.476(18) C3B-C4B 1.49(2) C4B-C5B 1.511(18) C5B-C6B 1.497(18) C6B-C7B 1.485(18) N1B-C7B 1.469(18)	N1B—C2B	1.420(15)		
C3BC4B 1.49(2) C4BC5B 1.511(18) C5BC6B 1.497(18) C6BC7B 1.485(18) N1BC7B 1.469(18)	C2B—C3B	1.476(18)		
C4B-C5B 1.511(18) C5B-C6B 1.497(18) C6B-C7B 1.485(18) N1B-C7B 1.469(18)	C3B—C4B	1.49(2)		
C5B-C6B 1.497(18) C6B-C7B 1.485(18) N1B-C7B 1.469(18)	C4B—C5B	1.511(18)		
C6B-C7B 1.485(18) N1B-C7B 1.469(18)	C5B—C6B	1.497(18)		
N1B—C7B 1.469(18)	C6B—C7B	1.485(18)		
	N1B—C7B	1.469(18)		

b)

Sb—Cl1	2.385(2)	Cl1—Sb—Cl2	89.25(4)
Sb—Cl2	2.516(1)	Cl1—Sb—Cl3	89.69(5)
Sb—Cl3	2.581(2)	Cl2—Sb—Cl3	87.33(4)
Sb—Cl4	2.672(2)	Cl1—Sb—Cl4	87.71(5)
Sb—Cl5	2.805(2)	Cl2—Sb—Cl4	87.81(4)
Sb—Cl4 ⁱ	3.401(2)	CI3—Sb—CI4	174.52(4)
		Cl1—Sb—Cl5	83.36(4)
N1A—C2A	1.493(7)	Cl2—Sb—Cl5	172.57(4)
C2A—C3A	1.494(8)	CI3—Sb—CI5	93.30(4)
C3A—C4A	1.499(9)	Cl4—Sb—Cl5	91.18(4)
C4A—C5A	1.55(2)	Cl1—Sb—Cl4 ⁱ	164.29(4)
C4A—C51A	1.42(3)	Cl2—Sb—Cl4 ⁱ	77.58(3)
C5A—C6A	1.39(2)	Cl3—Sb—Cl4 ⁱ	98.11(5)
C51A—C61A	1.27(4)	Cl4—Sb—Cl4 ⁱ	83.31(3)
C6A—C7A	1.511(13)	CI5—Sb—CI4 ⁱ	109.62(3)
C61A—C7A	1.483(14)		
N1A—C7A	1.512(7)		
N1B—C2B	1.487(6)		
C2B—C3B	1.510(8)		
C3B—C4B	1.505(8)		
C4B—C5B	1.518(8)		
C5B—C6B	1.520(8)		
C6B—C7B	1.517(8)		
N1B—C7B	1.505(7)		

Symmetry code: (i) x-1/2, -y+1/2, -z+1.

Table S3. Hydrogen-bond geometry [Å, °] for **HBC** at a) 300, b) 260 and c) 200 K.

a)

D—H···A	D—H	Н…А	D…A	D—H···A
O1 <i>H</i> −H2 <i>H</i> …Cl1	0.84	2.71	3.285(3)	128
O1 <i>H</i> −H1 <i>H</i> …Cl1 ⁱ	0.84	2.55	3.285(3)	147
O1 <i>H</i> −H2 <i>H</i> …Cl1 ⁱⁱ	0.84	2.71	3.285(3)	128
O1 <i>H</i> −H2 <i>H</i> …Cl2	0.84	2.76	3.273(3)	121
N1A—H1A2…Cl1 ⁱⁱ	0.89	2.76	3.56(4)	150
N1A—H1A1…Cl1 ⁱⁱⁱ	0.89	2.84	3.37(4)	120
C7A—H7A1…Cl1 ^{iv}	0.97	3.02	3.75(5)	133

b)

D—H···A	D—H	H···A	D···A	D—H…A	
O1 <i>H</i> —H2 <i>H</i> …Cl1	0.84	2.71	3.290(4)	128	
O1 <i>H</i> −H1 <i>H</i> …Cl1 ⁱ	0.84	2.56	3.290(4)	147	
01 <i>H</i> —H2 <i>H</i> …Cl1 ⁱⁱ	0.84	2.71	3.290(4)	128	
O1 <i>H</i> —H2 <i>H</i> …Cl2	0.84	2.75	3.262(4)	121	
N1A—H1A2…Cl1 ⁱⁱ	0.89	2.71	3.50(5)	149	
N1A—H1A1…Cl1 ⁱⁱⁱ	0.89	2.84	3.33(5)	117	
C7A—H7A1…Cl1 ^{iv}	0.97	2.93	3.70(4)	138	

c)

D—H···A	D—H	H···A	D···A	D—H…A	
O1 <i>H</i> −H2 <i>H</i> …Cl1	0.84	2.48	3.242(6)	152	
O1 <i>H</i> —H1 <i>H</i> …Cl2	0.84	2.61	3.241(2)	133	
01 <i>H</i> —H1 <i>H</i> …Cl3	0.84	2.81	3.334(5)	122	
N1A—H1A2…Cl2 ⁱ	0.91	2.66	3.505(7)	155	
N1A—H1A1…Cl3	0.91	2.44	3.300(8)	158	
C7A—H7A2…Cl3 ⁱ	0.99	2.82	3.581(10)	134	

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

Table S4. Selected bond lengths [Å] and angles [°] for HBC at a) 300 K, b) 260 and b) 200 K.

a)

b)

c)

Bi—Cl1	2.702(2)	Cl1—Bi—Cl2	89.14(7)
Bi—Cl1 ⁱ	2.702(2)	Cl1—Bi—Cl1 ⁱⁱⁱ	92.57(14)
Bi—Cl1 ⁱⁱ	2.702(2)	Cl1—Bi—Cl2 ⁱ	90.86(7)
Bi—Cl1 ⁱⁱⁱ	2.702(2)	Cl1 ⁱ —Bi—Cl1	180.0
Bi—Cl2	2.711(3)	Cl1 ⁱ —Bi—Cl1 ⁱⁱ	92.57(14)
Bi—Cl2 ⁱ	2.711(3)	Cl1 ⁱ —Bi—Cl1 ⁱⁱⁱ	87.43(14)
	(0)	$Cl1^i - Bi - Cl2$	90.86(7)
N1A—C7A	1 486(19)	$C 1^i - Bi - C 2^i$	89 14(7)
C2A-C3A	1 41(5)	$CI1^{ii}$ —Bi—CI1	87 43(14)
C3A - CAA	1 33(3)		180.0
C1A - C5A	1 42(2)		90.86(8)
C5A_C6A	1.45(3)		90.14(7)
	1.43(4)		85.14(7)
	1.42(5)		89.14(7)
NIA-CZA	1.49(4)		90.86(7)
			180.0
Ri—Cl1	2 697/2)		89 51(8)
	2.037(3)		03.31(0) 02 <i>11</i> (18)
	2.037(3)		92.44(10) 00.40(9)
	2.097(3)		90.49(8)
	2.697(3)		180.00(11)
	2.706(3)		92.44(18)
Bi—Cl2 ⁱ	2.706(3)	Cl1 ⁱ —Bi—Cl1 ⁱⁱⁱ	87.56(18)
		Cl1'—Bi—Cl2	90.49(8)
N1A—C2A	1.49(4)	Cl1 ⁱ —Bi—Cl2 ⁱ	89.51(8)
C2A—C3A	1.34(4)	Cl1"—Bi—Cl1	87.56(18)
C3A—C4A	1.39(3)	Cl1"—Bi—Cl1"	180.0
C4A—C5A	1.41(3)	Cl1 ⁱⁱ —Bi—Cl2	90.49(8)
C5A—C6A	1.48(4)	Cl1 ⁱⁱ —Bi—Cl2 ⁱ	89.51(8)
C6A—C7A	1.46(5)	Cl1 ⁱⁱⁱ —Bi—Cl2	89.51(8)
N1A—C7A	1.465(19)	Cl1 ⁱⁱⁱ —Bi—Cl2 ⁱ	90.49(8)
		Cl2—Bi—Cl2 ⁱ	180.0
BI-CI1	2.69/6(18)	CI1—BI—CI2	91.68(6)
Bi—Cl1	2.6976(18)	Cl1—Bi—Cl3	91.43(6)
Bi—Cl2	2.712(2)	Cl1—Bi—Cl2 ⁱ	88.32(6)
Bi—Cl2 ⁱ	2.712(2)	Cl1 ⁱ —Bi—Cl1	180.0
Bi—Cl3	2.7086(18)	Cl1 ⁱ —Bi—Cl3 ⁱ	91.43(6)
Bi—Cl3 ⁱ	2.7086(18)	Cl1 ⁱ —Bi—Cl3	88.57(6)
		Cl1 ⁱ —Bi—Cl2	88.32(6)
N1A—C2A	1.465(16)	Cl1 ⁱ —Bi—Cl2 ⁱ	91.68(6)
C2A—C3A	1.485(18)	Cl3 ⁱ —Bi—Cl1	88.57(6)
C2A—C31A	1.35(4)	Cl3—Bi—Cl3 ⁱ	180.0
C3A—C4A	1.474(17)	Cl3 ⁱ —Bi—Cl2	92.90(6)
C31A—C4A	1.46(4)	Cl3 ⁱ —Bi—Cl2 ⁱ	87.10(6)
C4A—C5A	1,494(15)	CI3 - Bi - CI2	87.10(6)
C5A—C6A	1 /67/16)		92 90(6)
CSA = COA	1.407(10)		190.0
	1.303(10)		100.0
	14/X(1b)		

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

Table S5. Hydrogen-bond geometry $[Å, \circ]$ for **HBB** at a) 280 and b) 200 K.

a)

D—H···A	D—H	H…A	D…A	D—H…A
N1A—H1A1…Br4	0.89	2.62	3.514(11)	178
N1A—H1A2…Br2 ⁱ	0.89	2.78	3.511(10)	141
N1 <i>B</i> —H1 <i>B</i> 1…Br2 ⁱ	0.89	2.61	3.461(10)	160
N1 <i>B</i> —H1 <i>B</i> 2…Br3	0.89	2.60	3.438(10)	157
C2A—H2A4…Br2 ⁱ	0.97	2.97	3.698(16)	133
C7A—H7A1…Br5	0.97	3.03	3.776(12)	135
C7A—H7A2…Br4 ⁱ	0.97	3.00	3.962(15)	171
C2 <i>B</i> —H2 <i>B</i> 1…Br4 ⁱⁱ	0.97	3.04	3.803(13)	136
C6 <i>B</i> —H6 <i>B</i> 1…Br1 ⁱⁱⁱ	0.97	2.97	3.708(11)	134

b)

D—H···A	D—H	H…A	D····A	D—H…A	
N1A—H1A1…Br4	0.89	2.62	3.512(10)	178	
N1A—H1A2…Br2 ⁱ	0.89	2.78	3.513(10)	141	
N1 <i>B</i> —H1 <i>B</i> 1…Br2 ⁱ	0.89	2.62	3.468(9)	159	
N1 <i>B</i> —H1 <i>B</i> 2…Br3	0.89	2.59	3.434(10)	158	
C2A—H2A4…Br2 ⁱ	0.97	2.98	3.704(15)	133	
C7A—H7A1…Br5	0.97	3.02	3.772(12)	135	
C7A—H7A2…Br4 ⁱ	0.97	3.00	3.964(15)	171	
C2B—H2B1…Br4 ⁱⁱ	0.97	3.04	3.801(12)	137	
C6B—H6B1…Br1 ⁱⁱⁱ	0.97	2.96	3.701(11)	134	

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

Table S6. Selected bond lengths [Å] and angles [°] for HBB at a) 280 K and b) 200 K.

a)

Bi—Br1	2.6893(12)	Br1—Bi—Br2	94.45(4)	
Bi—Br2	2.7844(13)	Br1—Bi—Br3	87.98(4)	
Bi—Br3	2.8171(14)	Br2—Bi—Br3	91.64(4)	
Bi—Br4	2.8819(14)	Br1—Bi—Br4	86.71(4)	
Bi—Br5	2.9416(13)	Br2—Bi—Br4	90.66(4)	
Bi—Br5 ⁱ	3.1256(13)	Br3—Bi—Br4	174.36(3)	
Br5—Bi ⁱⁱ	3.1256(13)	Br1—Bi—Br5	88.89(4)	
		Br2—Bi—Br5	176.62(3)	
N1A—C2A	1.450(15)	Br3—Bi—Br5	87.95(4)	
C2A—C3A	1.51(3)	Br4—Bi—Br5	90.06(3)	
C2A—C31A	1.32(4)	Br1—Bi—Br5 ⁱ	173.43(3)	
C3A—C4A	1.52(3)	Br2—Bi—Br5 ⁱ	91.55(4)	
C31A—C4A	1.50(4)	Br3—Bi—Br5 ⁱ	89.19(4)	
C4A—C5A	1.45(5)	Br4—Bi—Br5 ⁱ	95.90(4)	
C4A—C51A	1.41(5)	Br5—Bi—Br5 ⁱ	85.08(3)	
C5A—C6A	1.47(5)	Bi—Br5—Bi ⁱⁱ	158.31(4)	
C51A—C61A	1.47(5)			
C6A—C7A	1.54(3)			
C61A—C7A	1.47(3)			
N1A—C7A	1.470(15)			
N1B—C2B	1.504(15)			
С2В—С3В	1.427(17)			
C3B—C4B	1.549(18)			
C4B—C5B	1.503(18)			
C5B—C6B	1.509(17)			
С6В—С7В	1.452(15)			
N1B—C7B	1.495(13)			

b)

Bi—Br2	2.7142(10)	Br2—Bi—Br1	94.80(3)	
Bi—Br1	2.7559(10)	Br2—Bi—Br3	88.70(3)	
Bi—Br3	2.8234(11)	Br1—Bi—Br3	91.83(3)	
Bi—Br4	2.8758(11)	Br2—Bi—Br4	87.45(3)	
Bi—Br5 ⁱ	2.9618(10)	Br1—Bi—Br4	89.21(3)	
Bi—Br5	3.0669(11)	Br3—Bi—Br4	176.08(2)	
Br5—Bi ⁱⁱ	2.9619(10)	Br2—Bi—Br5 ⁱ	87.59(3)	
		Br1—Bi—Br5 ⁱ	177.61(3)	
N1A—C2A	1.495(11)	Br3—Bi—Br5 ⁱ	88.16(3)	
C2A—C3A	1.532(14)	Br4—Bi—Br5 ⁱ	90.96(3)	
C3A—C4A	1.495(15)	Br2—Bi—Br5	171.86(3)	
C4A—C5A	1.515(13)	Br1—Bi—Br5	93.24(3)	
C5A—C6A	1.536(14)	Br3—Bi—Br5	89.74(3)	
C6A—C7A	1.513(12)	Br4—Bi—Br5	93.97(3)	
N1A—C7A	1.503(11)	Br5 ⁱ —Bi—Br5	84.37(2)	
		Bi ⁱⁱ —Br5—Bi	153.46(3)	
N1B—C2B	1.526(11)			
C2B—C3B	1.513(12)			
C3B—C4B	1.509(13)			
C4B—C5B	1.538(12)			
C5B—C6B	1.483(12)			
C6B—C7B	1.541(12)			
N1B—C7B	1.487(11)			

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

Table S7. Comparison of the fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for **HBB** at 280 K and 200 K.

HBB 280 K	x	у	Ζ	$U_{\rm iso}^*/U_{\rm eq}$	Occ. (<1)	НВВ 200 К	x	У	Ζ	$U_{\rm iso}^*/U_{\rm eq}$
Bi	0.60866(2)	1.04806(4)	0.69171(2)	0.03770(14)		Bi	0.60920(2)	1.05002(3)	0.69467(2)	0.01870(12)
Br1	0.47513(7)	0.84206(14)	0.63323(5)	0.0556(3)		Br1	0.51515(7)	0.75262(10)	0.65692(4)	0.0293(2)
Br2	0.51408(9)	1.33852(13)	0.64801(5)	0.0621(3)		Br2	0.47126(6)	1.25803(11)	0.63781(4)	0.0297(2)
Br3	0.72702(9)	1.02925(14)	0.58170(5)	0.0584(3)		Br3	0.73082(7)	1.06177(11)	0.58345(4)	0.0309(2)
Br4	0.47801(8)	1.03743(13)	0.80002(5)	0.0553(3)		Br4	0.47694(7)	1.05655(10)	0.80442(4)	0.0278(2)
Br5	0.71855(8)	0.75348(14)	0.74071(5)	0.0562(3)		Br5	0.78302(6)	0.86099(11)	0.76217(4)	0.0286(2)
N1A	0.4616(7)	0.6035(14)	0.7767(5)	0.074(3)		N1A	0.4569(6)	0.4895(10)	0.7819(3)	0.0302(17)
C2A	0.3563(10)	0.559(2)	0.7649(7)	0.098(5)		C2A	0.3492(7)	0.5518(12)	0.7739(5)	0.039(2)
C3A	0.2855(17)	0.629(4)	0.8140(12)	0.082(7)	0.57(2)	C3A	0.2738(7)	0.4499(13)	0.8152(5)	0.044(3)
C31A	0.297(3)	0.506(4)	0.8103(19)	0.116(10)	0.43(2)					
C4A	0.2933(12)	0.549(2)	0.8797(8)	0.110(5)		C4A	0.2784(7)	0.4805(12)	0.8849(5)	0.038(2)
C5A	0.383(3)	0.517(4)	0.919(2)	0.103(8)	0.57(2)	C5A	0.3828(8)	0.4622(12)	0.9153(5)	0.038(2)
C51A	0.386(4)	0.578(4)	0.913(3)	0.084(8)	0.43(2)					
C6A	0.475(2)	0.592(4)	0.8925(11)	0.094(7)	0.57(2)	C6A	0.4591(8)	0.6020(13)	0.8951(5)	0.041(2)
C61A	0.466(3)	0.469(4)	0.8881(15)	0.078(8)	0.43(2)					
C7A	0.5166(9)	0.5222(18)	0.8299(6)	0.083(4)		C7A	0.5183(7)	0.5661(12)	0.8347(4)	0.033(2)
N1B	0.6873(7)	0.6049(13)	0.5796(4)	0.067(3)		N1B	0.6932(5)	0.4978(10)	0.5827(3)	0.0296(16)
C2B	0.7901(10)	0.5266(19)	0.5891(6)	0.091(4)		C2B	0.7968(7)	0.5851(13)	0.5922(4)	0.034(2)
C3B	0.8602(10)	0.551(2)	0.5392(7)	0.100(5)		C3B	0.8537(7)	0.6323(12)	0.5320(4)	0.034(2)
C4B	0.8485(10)	0.4311(19)	0.4815(7)	0.095(5)		C4B	0.8620(7)	0.4936(12)	0.4828(5)	0.034(2)
C5B	0.7544(10)	0.4475(17)	0.4402(6)	0.076(4)		C5B	0.7691(7)	0.4888(12)	0.4383(4)	0.032(2)
C6B	0.6574(10)	0.4524(14)	0.4768(6)	0.070(3)		C6B	0.6697(7)	0.4386(11)	0.4679(4)	0.031(2)
С7В	0.6402(9)	0.6023(16)	0.5140(5)	0.073(3)		C7B	0.6346(7)	0.5453(11)	0.5253(4)	0.034(2)

<u>PART 2</u>



Fig. S3. TGA and DTA scans for a) HSC, b) HSB, c) HBC and d)HBB.

The DSC results have shown that **HSC** (Fig. 1a) undergoes reversible phase transitions (PT) at 333/335 (cooling/heating, I \leftrightarrow II) with a thermal hysteresis ($\Delta T_{(I \leftrightarrow II)}$ = 2 K) and at 242 K (II \leftrightarrow III). The transition entropies for the transitions I \leftrightarrow II and II \leftrightarrow III are equal to $\Delta S_{(II \rightarrow II)}$ =7.80 J/mol·K and $\Delta S_{(III \rightarrow II)}$ =18.92 J/mol·K, respectively. It should be noted that the temperature hysteresis for the phase transition II \leftrightarrow III is very low, almost invisible, however, the value of $\Delta S_{(II \leftrightarrow III)}$ and peak shape present on the DSC curves clearly indicate the discontinuous nature (first-order) of this transformation.

In the case of **HSB**, we have found three solid-to-solid phase transitions. The reversible anomalies on the DSC runs for **HSB** at 281 K (I \leftrightarrow II), 266/270 K (cooling/heating, II \leftrightarrow III) and 258/264 K (cooling/heating, III \leftrightarrow IV) have been detected, see Fig. 1b. The shape of the small thermal anomaly between I and II phases is close to that characteristic of a continuous (or second-order) phase transition. The temperatures of the subsequent PTs, between II and IV phases, are a close one to the other. The entropy values of the thermal anomalies are equal to $\Delta S_{(III\rightarrowII)}=1.15$ and $\Delta S_{(IV\rightarrow III)}=9.95$ J/mol·K. The characteristics features of these anomalies, such as the presence of the thermal hysteresis ($\Delta T_{(III\leftrightarrow III)}=3$ and $\Delta T_{(III\leftrightarrow IV)}= 6$ K) and relatively large entropy values, indicate the discontinuous nature of these transformations.

From the DSC results for **HBC** one can state that four PTs have been revealed. The thermal anomalies on the DSC runs have been detected at the following temperatures 274/275 K (I \leftrightarrow II), 242/243 K (II \leftrightarrow III), 179/186 K (III \leftrightarrow IV) and 170/172 K (IV \leftrightarrow V), see Fig. 1c. All of the solid-to-solid phase transitions exhibit thermal hysteresis ($\Delta T_{(I \leftrightarrow II)} = 1$, $\Delta T_{(II \leftrightarrow III)} = 1$, $\Delta T_{(III \leftrightarrow IV)} = 7$ and $\Delta T_{(IV \leftrightarrow V)} = 2$ K) indicating the first-order PTs. The values of the transition entropies ($\Delta S_{(II \rightarrow II)} = 1.66$, $\Delta S_{(III \rightarrow II)} = 3.38$ and $\Delta S_{(V \rightarrow IV)} = 15.32$ J/mol·K) and shapes of the PTs peaks are another reason to qualify these phase transitions as discontinuous in nature.

In turn, in the case of **HBB**, the DSC data unambiguously reveal that the crystal undergoes a firstorder phase transition at 261/266 K (I \leftrightarrow II) with a thermal hysteresis ($\Delta T_{(I \leftrightarrow II)}$ = 5 K) (see, Fig. 1d). The entropy value, $\Delta S_{(II \rightarrow II)}$ is equal to 20.34 J/mol·K.

PART 3



Fig. S4. The temperature dependence of the imaginary part, ϵ'' , of the electric permittivity for the polycrystalline material of a) **HSC**, b) **HSB** and c) **HBC**.



Fig. S5. The plot of σ_{dc} versus 1000/T for a) **HSB**, b) **HBC** and c) **HBB** material in *log-log* scale.

<u>PART 4</u>

The temperature dependencies of the second moment, M_2 , of the proton resonance lines for HSC, HSB, HBC and HBB are shown in Fig. S6. There is no sudden drop in any PTs found for all studied samples. For HSC the second-moment values exhibit only one reduction, from about 51 G² at 120 K to 6 G² at 180 K (such a large value of M_2 at 120 K is amazing and may indicate the existence of a small real distance between some protons in the distorted cation rings at low temperatures). For HSB the second moment also drops once, from about 24 G² at 180 K to 5 G² at 280 K. At 180 K, a barely visible trace reduction of the second Moment M_2 is visible, which may be related to the observed dielectric dispersion – see Fig. 9b. For HBC the second-moment values reduce in two steps, first from about 32 G² at 125 K to 14 G² at 150 K, then to about 5 G² at 290 K. In addition, at 170K, the reduction of the second moment is clearly visible, which correlates perfectly with the phase transition observed, for example, in dielectric measurements – see Fig 9c. For HBB the second moment values, M_2 , also decreases in two steps, first from about 31.5 G² at 165 K to 27 G² at 190 K, then to about 10 G² at 280 K. Above 270 K the second moment, M_2 , for three studied compounds are similar and only for HBB is twice as large as for the other compounds, probably due to still existing limitations for the cationic motions even at such high temperatures.

The theoretical calculation of the dipolar second moment, M_2 , for the rigid structure obtained from the single-crystal X-ray diffraction experiment was carried out in the present paper using the equation derived by van Vleck [ref. ¹]:

$$M_{2} = \frac{3}{5}I(I+1)\gamma^{2}\mathsf{h}^{2}\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}R_{ij}^{-6},$$
(2)

where *N* is the number of protons in the unit cell, R_{ij} are distances between interacting protons. The calculation of the M₂ value for the rigid crystal structure has been performed using the distances typical in the NMR theoretical analysis and equal to 1.09, 1.03 and 0.97 Å for C—H, N—H and O—H, respectively. It should be noted that the positions of hydrogen nuclei have been theoretically assumed. The calculations yield the values between 21.2 G² and 24.4 G² for all four compounds. On the other hand for distances taken from the present XRD data the following M₂ values for the rigid states have been calculated: **HSC** – 34.7 G², **HSB** – 41.3 G², **HBC** – 43.4 G² and **HBB** – 33.8 G². The observed differences between the experimentally measured values of the second moment and the theoretical values determined from the probably does not take into account the influence of quadrupole interaction influence on the experimental

second-moment wave measurement. The quadrupole interactions have been already mentioned in the section devoted to the spin-lattice relaxation time, T_1 , analysis, as the dominating factor at low temperatures.



Figure S6. The temperature dependence of the second moment (M₂) of the proton NMR for **HSC**, **HSB**, **HBC** and **HBB**.

	E _a [kJ/mol] ([kcal/mol])	Temperature range for the E _a estimation [K]	τ _{c0} [s]	The relaxation constant C [s ⁻²]
HSC	19.7 (4.7)		2.4 10 ⁻¹⁴	$1.9 \cdot 10^{10}$
HSB	8.4 (2.0)	(110, 165)		
НВС	20.1 (4.8)		1.8 10-1	2.9·10 ¹⁰
HBB	4.6 (1.1)	(145, 240)		

Table S8. The ¹H NMR parameters for the spin-lattice relaxation times, T_1 .

<u>PART 5</u>

The standard experimental setup consists of Q-switched pulse laser working at fundamental wavelength λ =1.064 µm) and a fiber optics spectrometer for detecting doubled in frequency radiation at λ =532 nm produced by the investigated material in the form of fine powder. The fiber entrance aperture collects only a small portion of the SHG signal scattered in a wide angle from the sample excited by 1064 nm radiation. We used this technique to evaluate second order non-linear optical properties of **HSC** with respect to reference powder of the well-known highly optically non-linear KH₂PO₄ (KDP) crystal. The KDP coefficients mainly related to SGH are d₃₆ = 0.46 pm/V and d₁₄ = 0.43 pm/V at 1064 nm, which by definition are related with the second-order nonlinear susceptibility $\chi_{ijk}^{(2)}$ via $d_{ijk} \equiv (1/2) \cdot \chi_{ijk}^{(2)}$. In the powder SHG technique it is important that the grain size *r* of a powdered substance is greater than its coherence length

 l_c for SHG process, *i.e.* $l_c = \frac{\lambda}{4(n_{2\omega} - n_{\omega})}$. For KDP we prepared the powder sample of micro-crystals with grain size r of 80 to 120 \mathbb{D} m, which satisfies the mentioned above condition that $r > l_c$. The diameter of the laser spot of the infrared radiation incident on the sample was about 7 mm.

In the described SHG measurements of new material in a form of powder, we could not prepare the same grain size as for reference KDP crystal because the crystallites obtained from the synthesis have a needle-like morphology. Then we are not sure whether the condition that grain size $r > l_c$ is fulfilled (note that the refractive indices at 1064 nm and 532 nm are not known for this newly synthesized material so the coherence lengths for it is unknown). Both the reference material (KDP) and studied compound HSC were measured in the identical irradiation conditions and geometry of the light collection system that enabled us to compare its performance with respect to the KDP standard. For each powder sample we have performed measurement of SHG intensity versus incident pulse energy between 100 to 500 mJ, or until damage threshold. The laser pulse energy was controlled by the time delay of Pockels cell opening in the laser cavity with respect to the flash lamp pulse and measured with the laser energy meter. Taking the square root of the intensity of the SHG signal measured by a spectrometer with CCD detector digital dynamic range of 4096, we were able to calculate the SHG conversion efficiency factor for unknown materials. One must be aware of an error of this estimation as the grain sizes of measured substance to standard one were different. However, for the first evaluation of the material performance, this technique is able to confirm the non-centrosymmetricity of the compound and its ability to exhibit second-order nonlinear optical properties. Fig. S7 shows the plot of SHG signals in arbitrary units versus laser pulse energy. The inset shows the position of SH line exactly at 532 nm and its magnitude when excited with 350 mJ pulses (*i.e.* with a power density of 210 MW/cm²) of 1064 nm wavelength.



Figure S7. SHG at 532 nm wavelength obtained from the powder of **HSC** compound when excited by 10 ns, 380 mJ pulses of 1064 nm wavelength light delivered by Nd:YAG laser. The slope of the square root of SHG intensity with respect to laser pulse energy amounts to 0.0318 (mJ)⁻¹ (standard error 0.0024 (mJ)⁻¹).

The prolonged excitation of the studied compound with pulse energy exceeding 350 mJ leads to its optical damage and its SHG response decreases. The estimated from these experiments a damage threshold for 10 ns, 1064 nm laser light is near 200 MW/cm². The square root dependence of SHG intensity *versus* pulse energy performed for KDP powder under the same experimental conditions shows the slope of magnitude 0.202 (mJ)⁻¹. Then one can conclude that the SHG susceptibility of **HSC** is approximately 6 times smaller than that of KDP so averaged effective coefficient for **HSC** is $\langle d_{eff} \rangle = 0.072$ pm/V at 1064 nm. Estimated error of this measurement is ± 12 %.

References

1 J. H. Van Vleck, *Phys. Rev.*, 1948, **74**, 1168–1183.