

Electronic Supporting Information for:

**Structural, electric and dynamic properties of [pyrrolidinium]<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and [pyrrolidinium]<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub>; new lead-free organic-inorganic hybrids with narrow band gaps**

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**Table S1. Experimental details**

For all structures: crystal system orthorhombic, space group *Cmcm*,  $Z = 4$ . Experiments were carried out with Mo *K* $\alpha$  radiation using a Xcalibur, Atlas. Absorption was corrected for by multi-scan methods, *CrysAlis PRO* 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was implemented. H-atom parameters were constrained.

	(pyrrolidinium) <sub>3</sub> [Bi <sub>2</sub> I <sub>9</sub> ]	(pyrrolidinium) <sub>3</sub> [Sb <sub>2</sub> I <sub>9</sub> ]
<b>Crystal data</b>		
Chemical formula	Bi <sub>2</sub> I <sub>9</sub> ·2(C <sub>4</sub> H <sub>9.5</sub> N)·C <sub>4</sub> H <sub>10</sub> N	I <sub>9</sub> Sb <sub>2</sub> ·3(C <sub>4</sub> H <sub>10</sub> N)
$M_r$	1776.45	1601.99
Temperature (K)	230	240
$a, b, c$ (Å)	8.6726 (3), 18.1683 (8), 22.5902 (9)	8.5167 (5), 18.2142 (11), 22.6087 (19)
$V$ (Å <sup>3</sup> )	3559.5 (2)	3507.2 (4)
$\mu$ (mm <sup>-1</sup> )	17.69	9.47
Crystal size (mm)	0.33 × 0.21 × 0.18	0.25 × 0.18 × 0.07
<b>Data collection</b>		
$T_{\min}, T_{\max}$	0.370, 1.000	0.447, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	15444, 2437, 1484	17033, 2402, 1685
$R_{\text{int}}$	0.051	0.044
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.690	0.687
<b>Refinement</b>		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.052, 0.105, 1.02	0.053, 0.130, 1.07
No. of reflections	2437	2402
No. of parameters	59	63
No. of restraints	6	4
	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 57.7983P]$	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 60.7163P]$
	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.93, -0.98	1.17, -1.15

Computer programs: *CrysAlis PRO* 1.171.38.43 (Rigaku OD, 2015), *SHELXT* 2018/2 (Sheldrick, 2018), *SHELXL* 2018/3 (Sheldrick, 2015), *Olex2* 1.5 (Dolomanov *et al.*, 2009).

**Table S2. Selected geometric parameters (Å, °)**

(pyrrolidinium) <sub>3</sub> [Bi <sub>2</sub> I <sub>9</sub> ] 230 K		(pyrrolidinium) <sub>3</sub> [Sb <sub>2</sub> I <sub>9</sub> ] 240 K	
Bi1—I1 <sup>i</sup>	3.2429 (9)	Sb1—I2	3.2375 (12)
Bi1—I1	3.2429 (9)	Sb1—I3	3.2245 (9)
Bi1—I2	3.2458 (12)	Sb1—I3 <sup>i</sup>	3.2245 (9)
Bi1—I3	2.9498 (9)	Sb1—I4	2.8600 (9)
Bi1—I3 <sup>ii</sup>	2.9498 (9)	Sb1—I4 <sup>ii</sup>	2.8601 (9)
Bi1—I4	2.9505 (14)	Sb1—I5	2.8623 (14)
I1—Bi1—I1 <sup>i</sup>	83.63 (4)	I3 <sup>i</sup> —Sb1—I2	82.40 (3)
I1 <sup>i</sup> —Bi1—I2	81.89 (2)	I3—Sb1—I2	82.40 (3)
I1—Bi1—I2	81.89 (2)	I3—Sb1—I3 <sup>i</sup>	83.92 (3)
I3—Bi1—I1 <sup>i</sup>	89.95 (3)	I4 <sup>ii</sup> —Sb1—I2	92.36 (3)
I3 <sup>ii</sup> —Bi1—I1	89.95 (3)	I4—Sb1—I2	92.36 (3)
I3 <sup>ii</sup> —Bi1—I1 <sup>i</sup>	171.66 (3)	I4—Sb1—I3 <sup>i</sup>	89.67 (2)
I3—Bi1—I1	171.67 (3)	I4 <sup>ii</sup> —Sb1—I3	89.67 (2)
I3—Bi1—I2	91.97 (3)	I4—Sb1—I3	172.19 (3)
I3 <sup>ii</sup> —Bi1—I2	91.97 (3)	I4 <sup>ii</sup> —Sb1—I3 <sup>i</sup>	172.19 (3)
I3 <sup>ii</sup> —Bi1—I3	95.92 (5)	I4—Sb1—I4 <sup>ii</sup>	96.35 (5)
I3 <sup>ii</sup> —Bi1—I4	91.58 (3)	I4 <sup>ii</sup> —Sb1—I5	91.73 (3)
I3—Bi1—I4	91.58 (3)	I4—Sb1—I5	91.73 (3)
I4—Bi1—I1 <sup>i</sup>	94.18 (3)	I5—Sb1—I2	173.86 (4)
I4—Bi1—I1	94.18 (3)	I5—Sb1—I3 <sup>i</sup>	93.05 (3)
I4—Bi1—I2	174.70 (4)	I5—Sb1—I3	93.05 (3)
Bi1—I1—Bi1 <sup>iii</sup>	80.89 (3)	Sb1 <sup>iii</sup> —I2—Sb1	80.01 (4)
Bi1—I2—Bi1 <sup>iii</sup>	80.80 (4)	Sb1 <sup>iii</sup> —I3—Sb1	80.40 (3)

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

**Table S3. Experimental details 1 at rt**

(pyrrolidinium) <sub>3</sub> [Bi <sub>2</sub> I <sub>9</sub> ] RoomTemperature	
<b>Crystal data</b>	
Chemical formula	Bi <sub>2</sub> I <sub>9</sub> ·1.5(C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> )
<i>M<sub>r</sub></i>	1776.45
Crystal system, space group	Orthorhombic, <i>Cmcm</i>
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7266 (3), 18.1985 (8), 22.6661 (11)
<i>V</i> (Å <sup>3</sup> )	3599.6 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	17.49
Crystal size (mm)	0.22 × 0.18 × 0.07
<b>Data collection</b>	
Diffractionmeter	Xcalibur, Atlas
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.135, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	36050, 2014, 1621
<i>R</i> <sub>int</sub>	0.046
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.625
<b>Refinement</b>	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.047, 0.114, 1.17
No. of reflections	2014
No. of parameters	59
No. of restraints	5
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 63.0922P]$
	where $P = (F_o^2 + 2F_c^2)/3$
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	1.11, -1.06

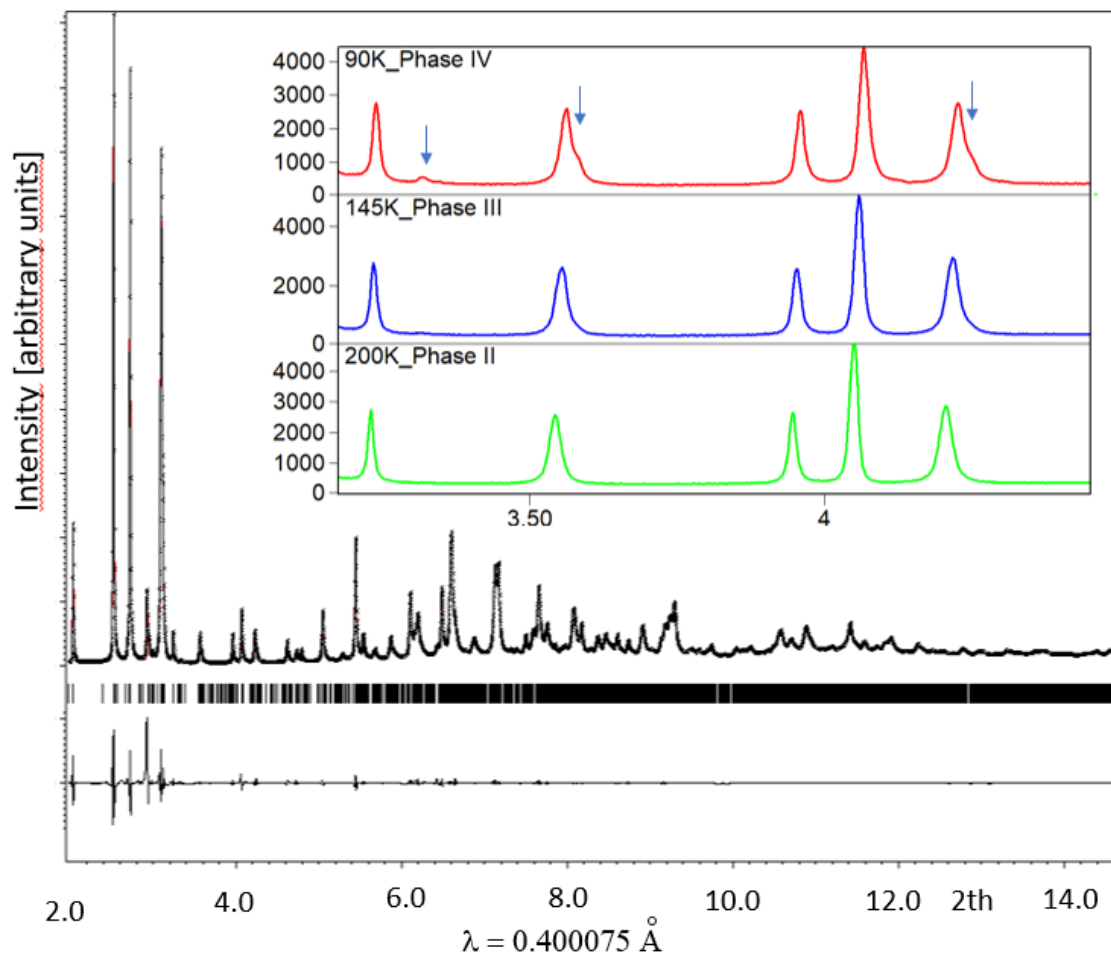
Computer programs: *CrysAlis PRO* 1.171.38.43 (Rigaku OD, 2015), *SHELXL* 2018/3 (Sheldrick, 2015), *Olex2* 1.5 (Dolomanov *et al.*, 2009).

**Table S4. Selected geometric parameters of 1 (Å, °)**

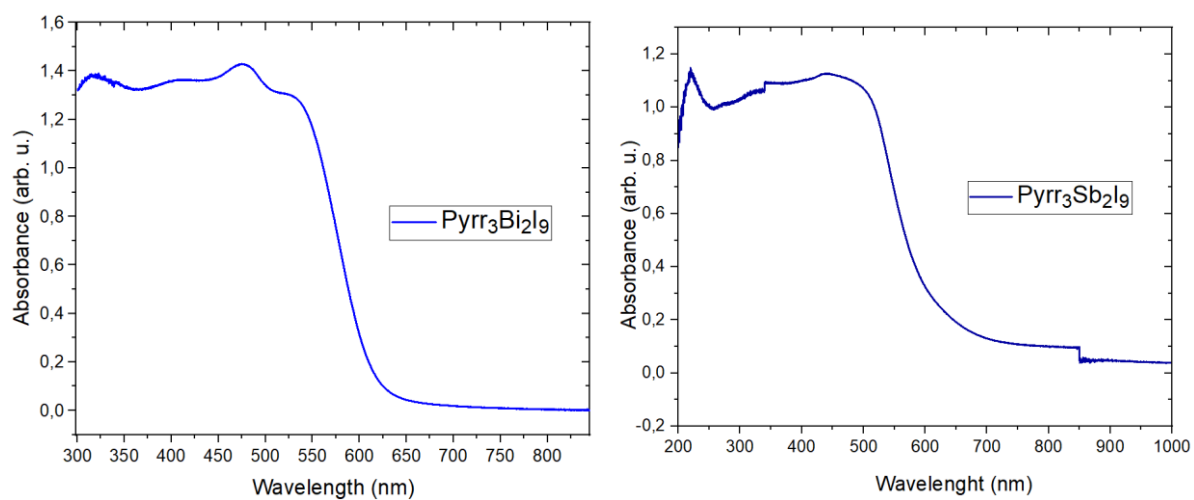
(pyrrolidinium) <sub>3</sub> [Bi <sub>2</sub> I <sub>9</sub> ] _room_temperature			
Bi1—I2	3.2413 (13)	Bi1—I4 <sup>ii</sup>	2.9513 (10)
Bi1—I3	3.2417 (10)	Bi1—I4	2.9513 (10)
Bi1—I3 <sup>i</sup>	3.2417 (10)	Bi1—I5	2.9517 (15)
I2—Bi1—I3	81.48 (3)	I4 <sup>ii</sup> —Bi1—I4	95.90 (5)
I2—Bi1—I3 <sup>i</sup>	81.48 (3)	I4 <sup>ii</sup> —Bi1—I5	91.67 (3)
I3—Bi1—I3 <sup>i</sup>	83.46 (4)	I4—Bi1—I5	91.67 (3)
I4—Bi1—I2	92.03 (3)	I5—Bi1—I2	174.48 (4)
I4 <sup>ii</sup> —Bi1—I2	92.03 (3)	I5—Bi1—I3	94.42 (4)
I4 <sup>ii</sup> —Bi1—I3 <sup>i</sup>	171.39 (3)	I5—Bi1—I3 <sup>i</sup>	94.42 (4)

I4 <sup>ii</sup> —Bi1—I3	90.01 (3)	Bi1—I2—Bi1 <sup>iii</sup>	81.31 (4)
I4—Bi1—I3	171.39 (3)	Bi1 <sup>iii</sup> —I3—Bi1	81.30 (3)
I4—Bi1—I3 <sup>i</sup>	90.01 (3)		

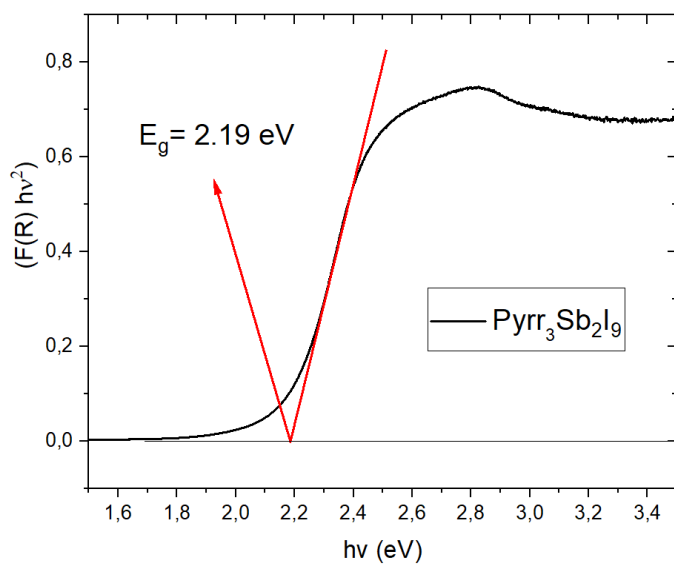
Symmetry code(s): (i)  $-x+1, y, -z+3/2$ ; (ii)  $-x+1, y, z$ ; (iii)  $x, y, -z+3/2$ .



**Figure S1.** *Le Bail* profile refinement results for SXRD data collected for **1** – (pyrrolidinium)<sub>3</sub>[Bi<sub>2</sub>I<sub>9</sub>] at 90 K; **Phase IV**;  $a=8.6027(1)\text{\AA}$ ,  $b=18.1808(3)\text{\AA}$ ,  $c=45.14445(7)\text{\AA}$ ,  $\alpha=90.061(1)$ ,  $\beta=90.878(2)$ ,  $\gamma=90.378(2)$ ,  $R_p=0.031$ ,  $wR_p=0.059$ . The inset shows the comparison between selected peaks of Phase II, III and IV. The arrows mark new intensities that appear in Phase IV.

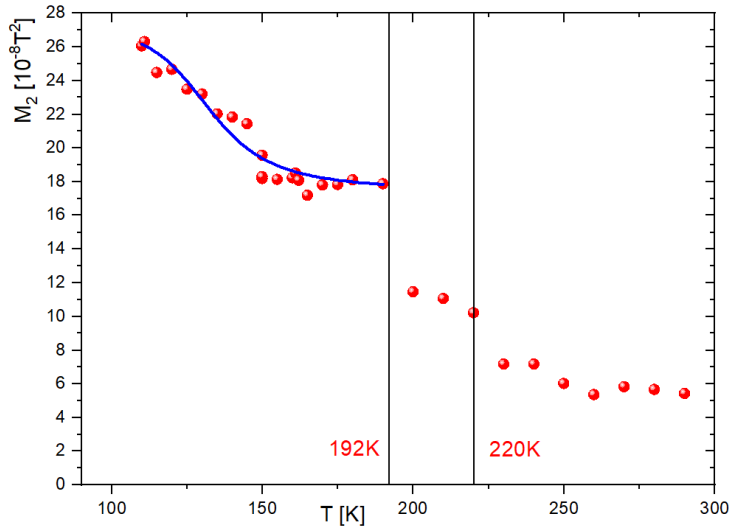


**Figure S2.** Diffuse reflectance spectra of **1** (left) and **2** (right)



**Figure S3.** Band gap ( $E_g$ ) estimation for **2** with Tauc plot

### Proton Magnetic Resonance ( $^1\text{H}$ NMR)



**Figure S4.**  $M_2$  Temperature dependence of second moment of  $^1\text{H}$  NMR line of **1**

Figure S4 depicts the temperature dependencies of the second moment  $M_2$  of the  $^1\text{H}$  NMR line of **1**. The  $M_2$  measurements reveal the detected phase transitions (PTs) observed through DSC and dielectric studies, as evidenced by a rapid reduction of the NMR line. The theoretical value of the second moment for a rigid lattice was calculated using the van Vleck formula [1]:

$$M_2 = \frac{3}{5} I(I+1) \gamma_H^2 \hbar^2 \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N R_{ij}^{-6},$$

where  $I$  represents the hydrogen nuclei spin,  $\gamma_H$  denotes the gyromagnetic ratio of proton spin ( $\gamma_H = 26.75221 \times 10^7 \text{ rad/Ts}$ ),  $R_{i,j}$  indicate the internuclear distance in the whole sample, and  $N$  refers to the number of resonant spins in the molecule. The computed value of the second moment for a rigid molecule ( $M_{2\text{rigid}}$ ) was determined to be  $22.14 \times 10^{-8} \text{ T}^2$ , which is lower than the measured value. For temperatures up to the PT at 192 K, the reduction of the second moment can be analyzed based on the BPP formula [2]:

$$M_2 = M_2 + (M_2 + M_2) \frac{2}{\pi} \arctg(\gamma_H \sqrt{M_2} \tau_c)$$

where the correlation time follows the Arrhenius law  $\tau_c = \tau_0 \exp(E_a/RT)$ ,  $M_{2\text{rigid}}$  and  $M_{2\text{motion}}$  represent the second moment values before (rigid) and after (motion) the onset of a given motion, respectively. Fitting the data yields the following parameters:  $E_a = 10.1 \text{ kJ/mol}$  and  $\tau_{c0}$

$= 8.04 \cdot 10^{-10}$  s (as shown by the fitting dotted curve in Fig. M2). Notably, in the vicinity of the PT at 192 K, a significant reduction of the second moment from  $18 \cdot 10^{-8} T^2$  to  $12 \cdot 10^{-8} T^2$  is observed, confirming a significant increase of the dynamics of the pyrrolidinium cations, the next drop is observed around 220 K. However, the value of  $M_2 \sim 5.5 \cdot 10^{-8} T^2$  in the HT phase indicates that pyrrolidinium cations do not follow free rotations.

[1] J.H. Van Vleck, Phys. Rev., 1948, 74, 1168

[2] N. Bloembergen, E.M. Purcell, R.V. Pond, Phys. Rev., 1948, 73, 679