

## Supramolecular diiodine-bromostannate(IV) complexes: narrow bandgap semiconductors

Nikita A. Korobeynikov, Andrey N. Usoltsev, Pavel A. Abramov, Maxim N. Sokolov and Sergey A. Adonin\*

**Table S1. Experimental details**

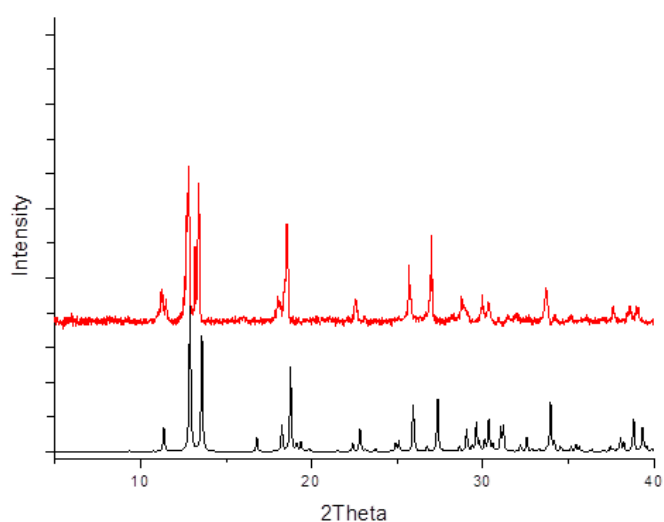
|  | <b>1</b>  | <b>2</b>   | <b>3</b>   |
|--|---|--|--|
| Chemical formula   | C <sub>8</sub> H <sub>24</sub> Br <sub>6</sub> I <sub>2</sub> N <sub>2</sub> Sn | C <sub>12</sub> H <sub>16</sub> Br <sub>6</sub> I <sub>2</sub> N <sub>2</sub> Sn   | C <sub>12</sub> H <sub>16</sub> Br <sub>6</sub> I <sub>2</sub> N <sub>2</sub> Sn |
| <i>M<sub>r</sub></i>   | 1000.23   | 1040.22  | 1040.22  |
| Crystal system, space group  | Tetragonal, <i>I</i> 4 <sub>1</sub> <i>cd</i>                                   | Tetragonal, <i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2   | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>                                   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 19.4249 (4), 19.4249 (4), 26.0612 (8)   | 9.6792 (2), 9.6792 (2), 25.5585 (8)  | 12.8268 (7), 14.5857 (7), 13.1741 (6)  |
| $\alpha$ , $\beta$ , $\gamma$ (°)  | 90, 90, 90  | 90, 90, 90   | 90, 107.082 (5), 90  |
| <i>V</i> (Å <sup>3</sup> )   | 9833.6 (5)  | 2394.50 (12)   | 2356.0 (2)   |
| <i>Z</i>   | 16  | 4  | 4  |
| $\mu$ (mm <sup>-1</sup> )  | 13.30   | 13.66  | 13.88  |
| Crystal size (mm)  | 0.10 × 0.10 × 0.07  | 0.20 × 0.15 × 0.05   | 0.25 × 0.20 × 0.20   |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>  | 0.661, 1.000  | 0.478, 1.000   | 0.759, 1.000   |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 13180, 5187, 4466   | 6889, 2724, 2439   | 10940, 5237, 4421  |
| <i>R</i> <sub>int</sub>  | 0.029   | 0.029  | 0.025  |
| $\theta$ values (°)  | $\theta_{\max} = 29.0$ ,<br>$\theta_{\min} = 2.1$                               | $\theta_{\max} = 29.1$ , $\theta_{\min} = 2.3$   | $\theta_{\max} = 29.1$ , $\theta_{\min} = 2.0$                                   |
| (sin $\theta$ /λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.682   | 0.684  | 0.685  |
| Range of <i>h</i> , <i>k</i> , <i>l</i>  | -25 ≤ <i>h</i> ≤ 19<br>-24 ≤ <i>k</i> ≤ 15<br>-34 ≤ <i>l</i> ≤ 32               | -12 ≤ <i>h</i> ≤ 8<br>-11 ≤ <i>k</i> ≤ 8<br>-25 ≤ <i>l</i> ≤ 31  | -17 ≤ <i>h</i> ≤ 16<br>-17 ≤ <i>k</i> ≤ 19<br>-11 ≤ <i>l</i> ≤ 17                |
| <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> | 0.030, 0.071, 1.07  | 0.025, 0.036, 0.98   | 0.031, 0.065, 1.11   |
| No. of reflections, parameters, restraints   | 5183, 216, 1  | 2724, 106, 0   | 5237, 208, 0   |
| Weighting scheme   | $w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$<br>where $P = (F_o^2 + 2F_c^2)/3$        | $w = 1/[\sigma^2(F_o^2) + (0.0071P)^2]$<br>where $P = (F_o^2 + 2F_c^2)/3$  | $w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$<br>where $P = (F_o^2 + 2F_c^2)/3$        |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )   | 1.00, -1.02   | 0.55, -0.56  | 0.83, -0.96  |
| Absolute structure   | Refined as an inversion twin.   | Flack <i>x</i> determined using 830 quotients [( <i>I</i> <sup>+</sup> )-( <i>I</i> <sup>-</sup> )]/[( <i>I</i> <sup>+</sup> )+( <i>I</i> <sup>-</sup> )] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). | —  |
| Absolute structure parameter   | 0.484 (13)  | 0.008 (9)  | —  |

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), *ShelXle* (Hübschle, 2011), *CIFTAB-2014* (Sheldrick, 2014).

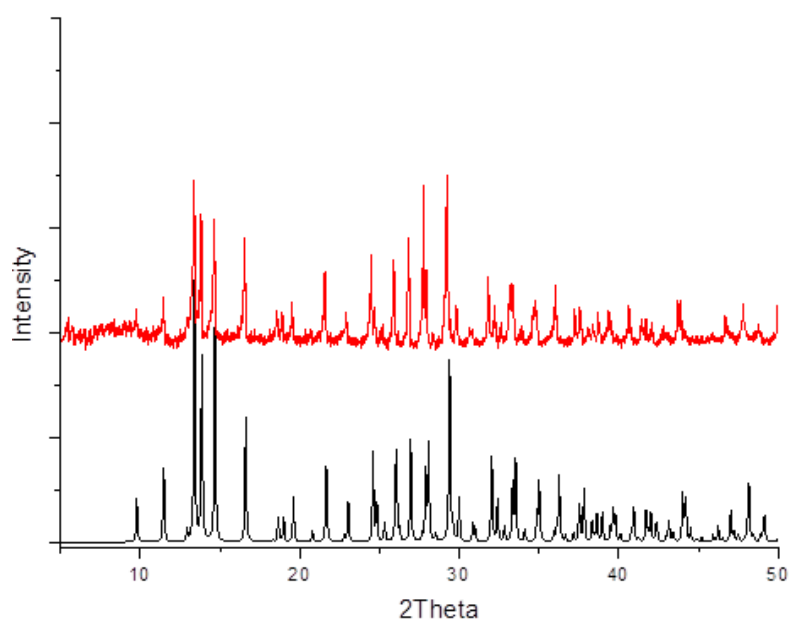
**Table S2. Selected geometric parameters (Å)**

| (1) main component |             | (2)                |             | (3)     |            |
|--------------------|-------------|--------------------|-------------|---------|------------|
| Br1—Sn1            | 2.6434 (12) | Br1—Sn1            | 2.5624 (10) | Br1—Sn1 | 2.6848 (5) |
| Br2—Sn1            | 2.6444 (12) | Br2—Sn1            | 2.5872 (5)  | Br2—Sn1 | 2.5994 (5) |
| Br3—Sn1            | 2.5917 (13) | Br3—Sn1            | 2.6272 (6)  | Br3—Sn1 | 2.5812 (6) |
| Br4—Sn1            | 2.5862 (14) | Br4—Sn1            | 2.6029 (10) | Br4—Sn1 | 2.6074 (6) |
| Br5—Sn1            | 2.5868 (12) | I1—I1 <sup>i</sup> | 2.7031 (8)  | Br5—Sn1 | 2.5629 (6) |
| Br6—Sn1            | 2.5882 (11) |                    |             | Br6—Sn1 | 2.5761 (5) |
| I1—I2              | 2.6916 (9)  |                    |             | I1—I2   | 2.6864 (5) |
| I3—I4              | 2.69 (5)    |                    |             |         |            |

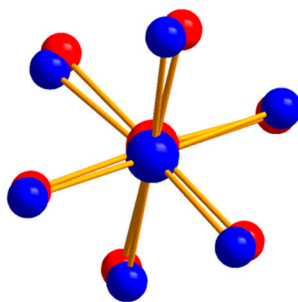
Symmetry code(s): (i)  $-y, -x, -z+3/2$ .



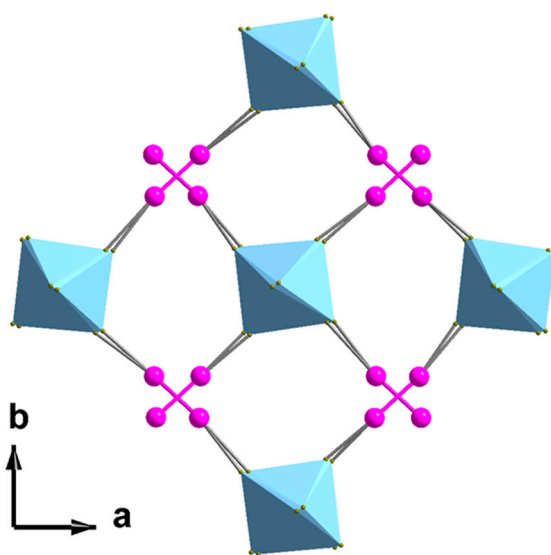
**Figure S1.** Calculated (*black*) and experimental (*red*) PXRD patterns of **1**



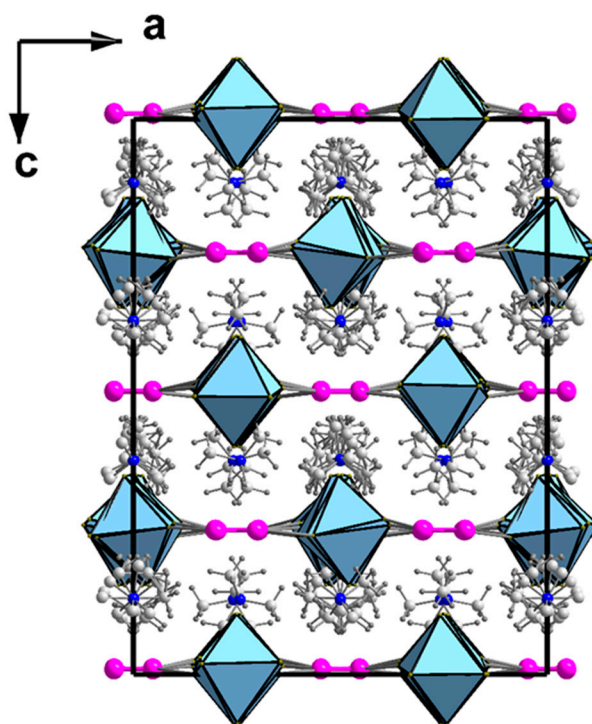
**Figure S2.** Calculated (*black*) and experimental (*red*) PXRD patterns of **2**



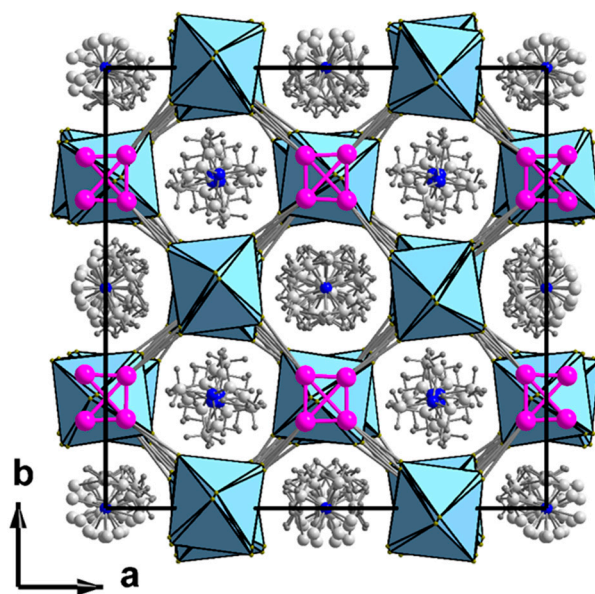
**Figure S3.** Positional disordering of  $[\text{SnBr}_6]^{2-}$  octahedron over two closed positions with 0.92 (red) and 0.08 (blue) occupancies.



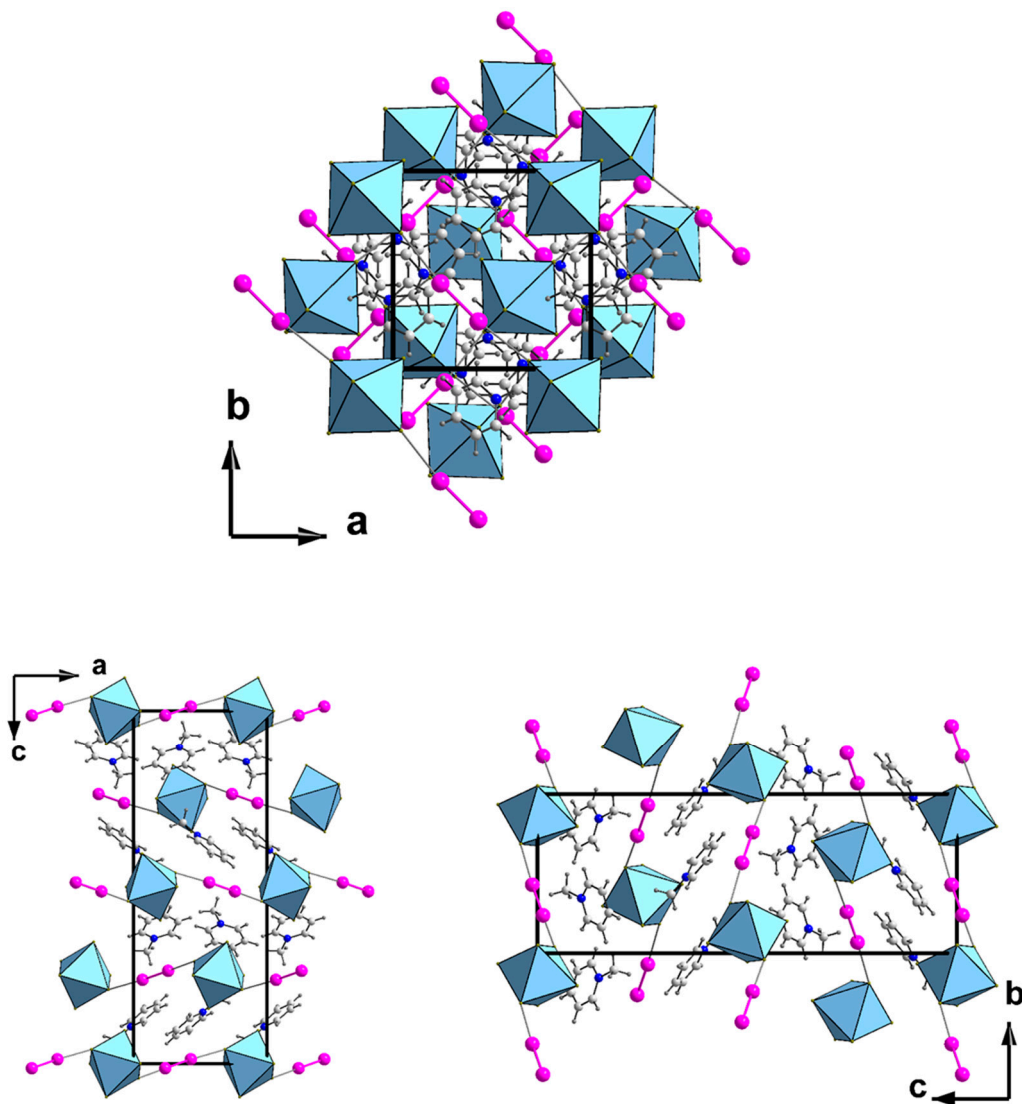
**Fig. S4.** Structure of the layer formed by  $[\text{SnBr}_6]^{2-}$  and  $\text{I}_2$  units



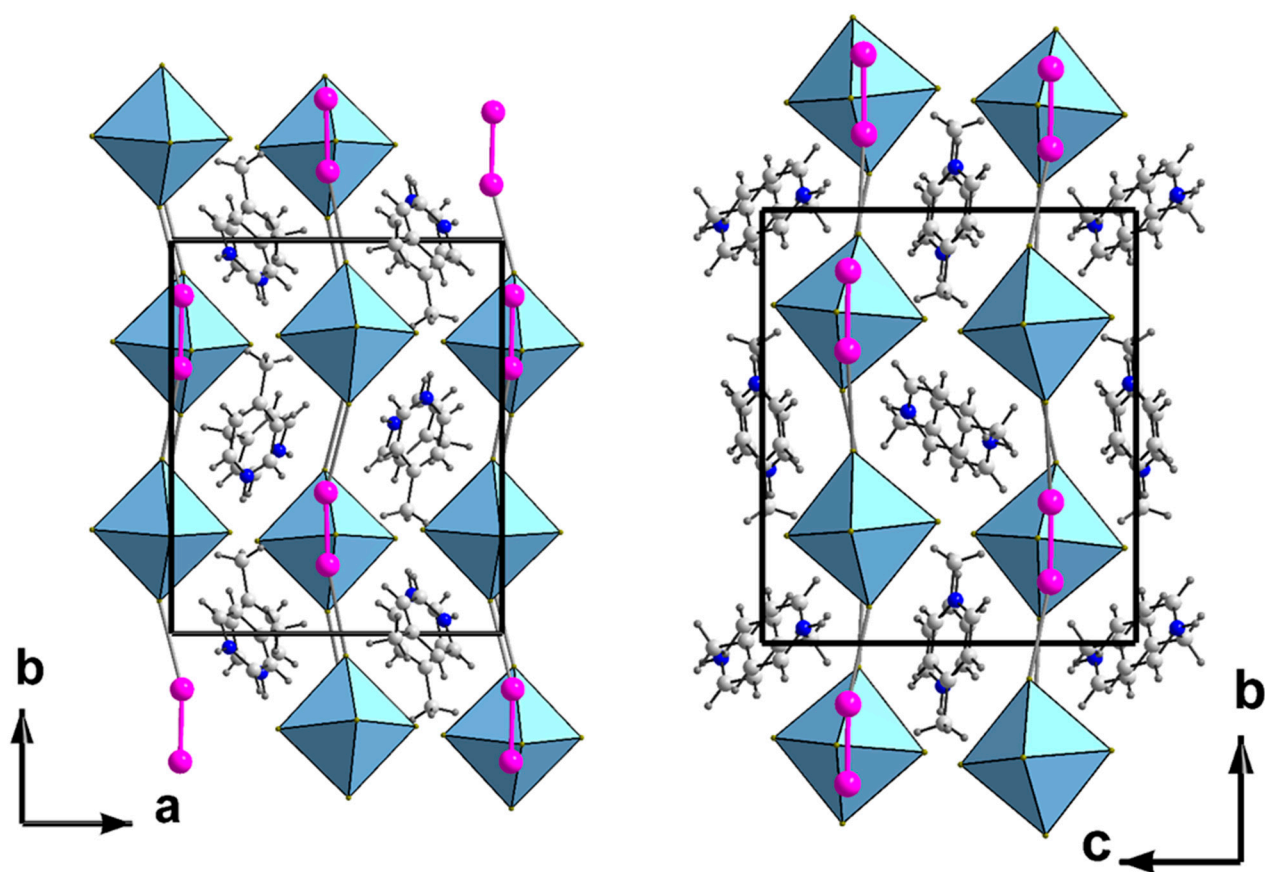
**Figure S5.** Layered crystal packing of **1**.



**Figure S6.** Positions of TMA<sup>+</sup> cations in the void between  $\{[\text{SnBr}_6]^{2-} + \text{I}_2\}$  nets



**Figure S7.** Crystal packing of **2**



**Figure S8.** Crystal packing of **3**