

# [BMIm]<sub>4</sub>[Sn<sub>9</sub>Se<sub>20</sub>]: Ionothermal Synthesis of a Selenidostannate with a 3D Open-framework Structure

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**SUPPORTING INFORMATION**

## Experimental Methods

### 1. Synthesis

K<sub>2</sub>Se and [K<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>][SnSe<sub>4</sub>] were synthesized according to literatures.<sup>[1]</sup> MnCl<sub>2</sub>·4H<sub>2</sub>O (>98%), and 1-butyl-3-methyl-imidazolium tetrafluoroborate [BMIm][BF<sub>4</sub>] (>98%) were purchased from Merck or Sigma-Aldrich used without purification.

To prepare compound [BMIm]<sub>4</sub>[Sn<sub>9</sub>Se<sub>20</sub>] **1** : *Method I* : A Teflon-lined autoclave (volume 23 mL) was charged with [K<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>][SnSe<sub>4</sub>] (0.133 g, 0.20 mmol) and [BMIm][BF<sub>4</sub>] (0.7 mL) in glovebox. The stainless steel autoclave was then sealed and heated to 130°C for 7 days. After cooling to room temperature red crystals were obtained. (Yield: 0.045 g, 63% *rsp* Sn). The similar synthesis procedures are also employed at heating to 150°C for 6 days or 180°C for 4 days, giving yields of **1** (0.048 g, 68% *rsp* Sn) and (Yield: 0.030 g, 42% *rsp* Sn), respectively. *Method II*: A Teflon-lined autoclave (volume 23 mL) was charged with K<sub>2</sub>Se (0.100 g, 0.64 mmol), Sn (0.050g, 0.42 mmol), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.040 g, 0.20 mmol) and [BMIm][BF<sub>4</sub>] (0.7 mL) in glovebox. The stainless steel autoclave was then sealed and heated to 160°C for 6 days. After cooling to room temperature red crystals were obtained by filtration, washed several times with deionized water and ethanol, and dried under air. (Yield: 0.068 g, 66% *rsp* Se). Elemental anal. Calcd: N, 3.50; C, 11.99; H, 1.89. Found: N, 3.47; C, 12.05; H, 1.78.

### 2. Energy dispersive X-ray spectroscopy (EDX analyses)

EDX-analyses were performed using the EDX-device Voyager 4.0 of Noran Instruments coupled with the electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. For the analyses multiple single crystals were used and the data recorded both: various times on one single crystal and various times on other single crystals. The radiation emitted by the atoms was analyzed: Sn-L, Se-K, Se-L (Figure S2).

### 3. Single crystal X-ray crystallography

Data of the X-ray structural analyses: T = 193 K, Mo-K<sub>α</sub>-radiation ( $\lambda_{\text{Mo-K}\alpha} = 0.71073$  Å), graphite monochromator, imaging plate detector STOE IPDS 2T. Structure solution by direct methods, full-matrix-least-squares refinement against F<sub>2</sub>; software used: SHELXS-97 and SHELXL-97<sup>[2]</sup>.

[C<sub>32</sub>H<sub>60</sub>N<sub>8</sub>Se<sub>20</sub>Sn<sub>9</sub>] (**1**, Figure S3). 3204.29 g·mol<sup>-1</sup>, monoclinic, space group *Cc*, red crystal, 0.25×0.18×0.06 mm<sup>3</sup>, *a* = 19.901(5) Å, *b* = 26.494(6) Å, *c* = 14.477(4) Å,  $\beta$  = 105.34(3)°, *V* = 7361(3) Å<sup>3</sup>, *Z* = 4,  $\rho(\text{calc.}) = 2.892$  g·cm<sup>-3</sup>,  $2\theta = 1.91 - 54.78^\circ$ , 33332 reflections collected, 12122 independent reflections [*R*<sub>int</sub> = 0.0833], 10292 with *I* > 2 $\sigma$ (*I*);  $\mu(\text{MoK}\alpha) = 12.919$  mm<sup>-1</sup>, 538 parameters. Refinement of all Se, Sn, and non-disordered C, N atoms in the imidazolium ions employing anisotropic displacement parameters; the C and N atoms in one of imidazolium ions were located from the difference-Fourier maps and refined with restraints (DFIX and ISOR ) to obtain chemical-reasonable models; another imidazolium ions are heavily disordered, which were refined isotropically with two parts of half occupancy factors by restraints

(DFIX, FLAT, EADP, EXYZ and FREE). Refinement of disordered C and N atomic sites employing isotropic displacement parameters; H atoms not calculated). Highest/deepest differential peak/hole: 1.08/−1.20 e<sup>−</sup>·Å<sup>−3</sup>. Refinement as racemic twin (BASF: 0.2513). GOF: 1.011. *R* values: *R*<sub>1</sub> = 0.0432 (for *I* > 2θ(*I*), based on *F*), *wR*<sub>2</sub> = 0.0973 (all data, based on *F*<sup>2</sup>).

[C<sub>32</sub>H<sub>60</sub>N<sub>8</sub>Se<sub>14</sub>Sn<sub>6</sub>] ([BMim]<sub>2</sub>[Sn<sub>3</sub>Se<sub>7</sub>], CCDC 828309). 2374.46 g·mol<sup>−1</sup>, monoclinic, space group *Cc*, orange block, 0.20×0.15×0.12 mm<sup>3</sup>, *a* = 13.938(3) Å, *b* = 24.075(5) Å, *c* = 18.854(4) Å, β = 106.25(3)°, *V* = 6074(2) Å<sup>3</sup>, *Z* = 4, ρ(calc.) = 2.597 g·cm<sup>−3</sup>, 2θ = 1.91 – 54.78°, 35447 reflections collected, 10683 independent reflections [*R*<sub>int</sub> = 0.0855], 10345 with *I* > 2θ(*I*); μ(MoK<sub>α</sub>) = 10.851 mm<sup>−1</sup>, 596 parameters. Refinement of all atoms employing anisotropic displacement parameters; H atoms not calculated. Highest/deepest differential peak/hole: 1.33/−1.64 e<sup>−</sup>·Å<sup>−3</sup>. Flack parameter: 0.013(7). GOF: 1.012. *R* values: *R*<sub>1</sub> = 0.0337 (for *I* > 2θ(*I*), based on *F*), *wR*<sub>2</sub> = 0.0852 (all data, based on *F*<sup>2</sup>).

The crystals of [EMim]<sub>2</sub>[Sn<sub>3</sub>Se<sub>7</sub>], also quoted in the manuscript, systematically show heavy twinning problems and do not allow for a complete refinement beyond the identification of the network structure. Therefore, the data are not presented here.

#### 4. X-ray powder diffraction

Data collection was performed on an X-ray powder diffractometer (CuK<sub>α</sub> graphite monochromatized radiation) operating at 40kV/40mA and equipped with a position-sensitive detector with flat sample geometry. The samples were prepared by grinding the crystals to a powder and spreading it on a sample holder (Figures S5, S6 and S7).

#### 5. Thermogravimetric analyses

TGA data (Figures S8, S9) were collected on NETZSCH STA 409 CD device under Ar atmosphere with the following settings: temp. range 25-500°C, scanning rate 5 K/min (Figure S8) and temp. range 25-800°C, scanning rate 5 K/min.

#### 6. UV-Vis spectroscopy

The UV-VIS spectrum (Figure S10) was recorded on a Perkin Elmer Cary 5000 UV/Vis/NIR spectrometer in the range of 800–200 nm employing double beam technique. The samples were measured as suspensions in nujol oil between two quartz plates and rapidly brought into the UV-VIS beam.

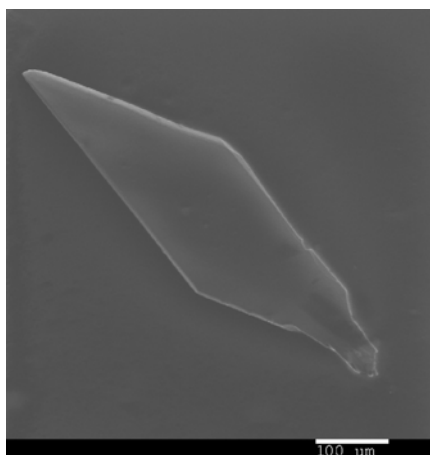
#### 7. Raman Spectroscopy

Raman spectrum was recorded on a Labram HR 800 Raman spectrometer with a 632.8 nm red laser in the range of 50-3000 cm<sup>−1</sup>. The beam was focused on the sample through a confocal microscope using a 50× objective lens.

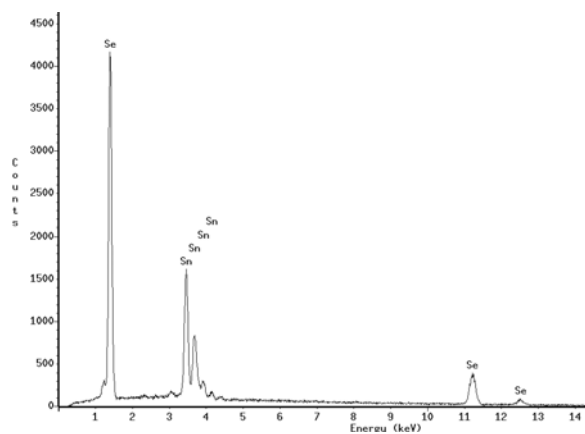
#### 8. References

- (1) Ruzin, E. PhD thesis, Marburg, Germany, 2007.
- (2) Sheldrick, G. M., SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA, 1997.

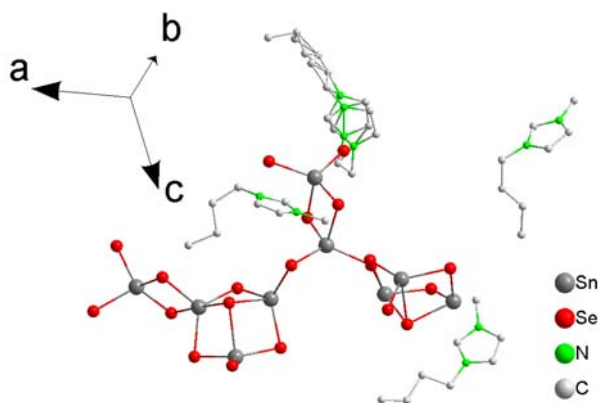
## Supplementary Figures



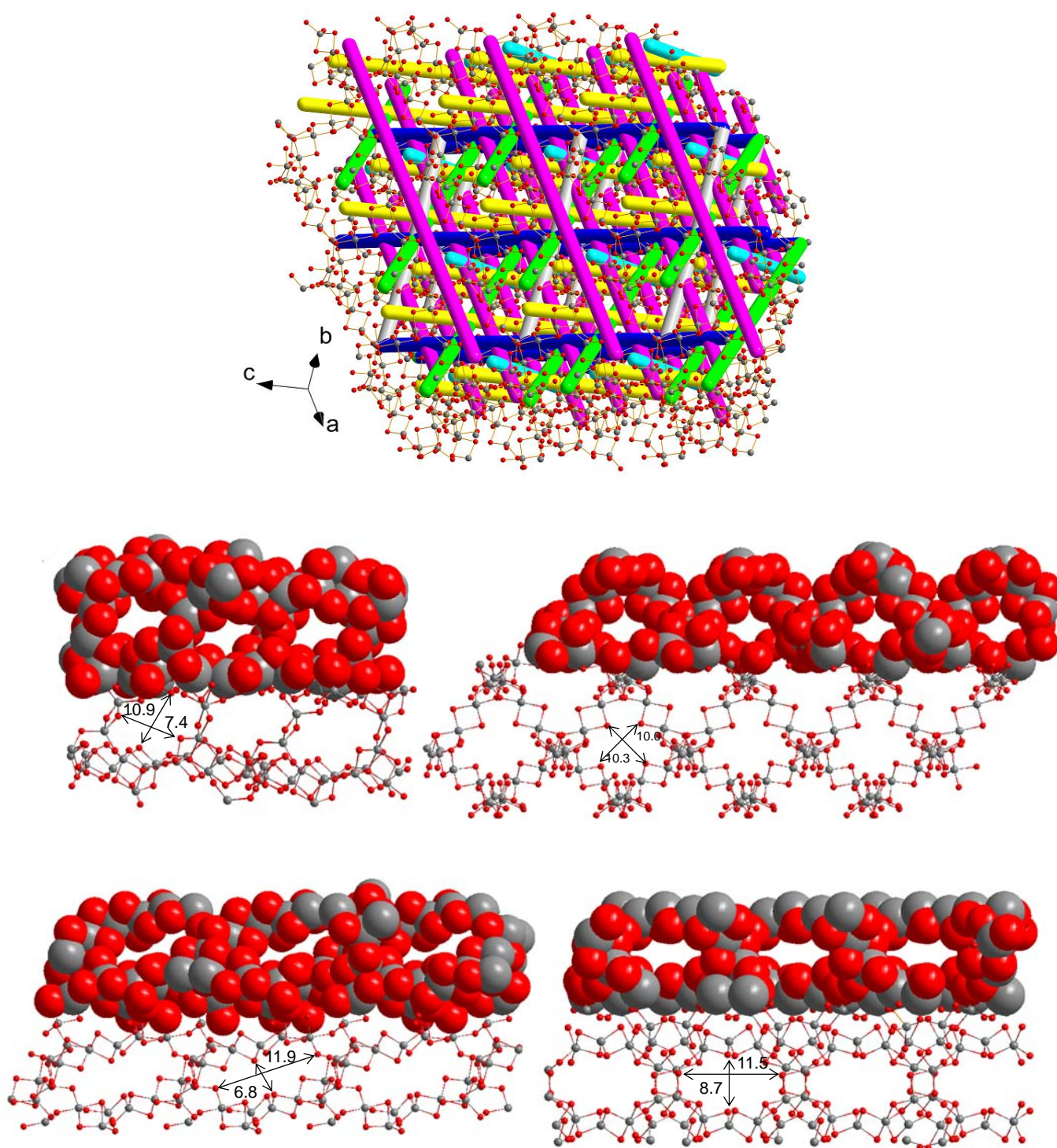
**Figure S1.** SEM image of a single crystal of [BMIm]<sub>4</sub>[Sn<sub>9</sub>Se<sub>20</sub>] (**1**).



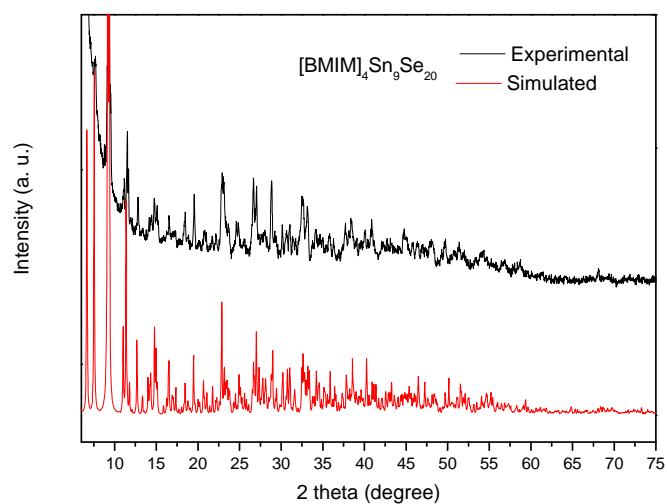
**Figure S2.** EDX analysis of compound **1**. Sn : Se = 1 : 2.22 (calculated);  
Sn : Se = 1 : 2.19 (EDX)



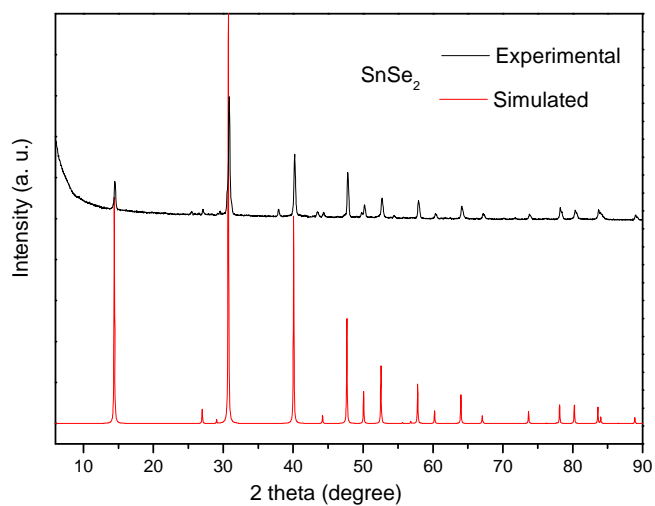
**Figure S3.** Crystallographically asymmetric unit in compound **1**, [BMIm]<sub>4</sub>[Sn<sub>9</sub>Se<sub>20</sub>].  
Hydrogen atoms are omitted for clarity.



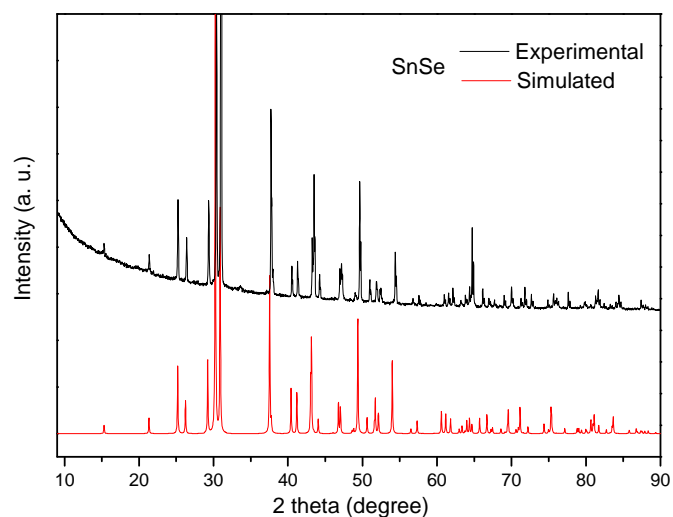
**Figure S4.** Summary of all channels running through the crystal structure of **1** illustrated as sticks of different colors (top). Illustration of the channels in **1** that run along [112] (center left), [100] (center right), [110] (bottom left), and [101] (bottom right). Measures are given in Å. The [BMIm]<sup>+</sup> cations that are located in the channels are omitted for clarity. Grey, Sn; red, Se.



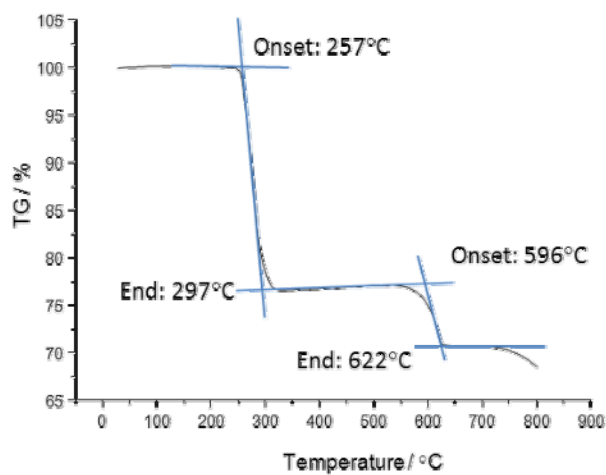
**Figure S5.** Powder X-ray diffraction pattern of compound **1** and a simulated pattern based on the single crystal data XRD pattern of **1**.



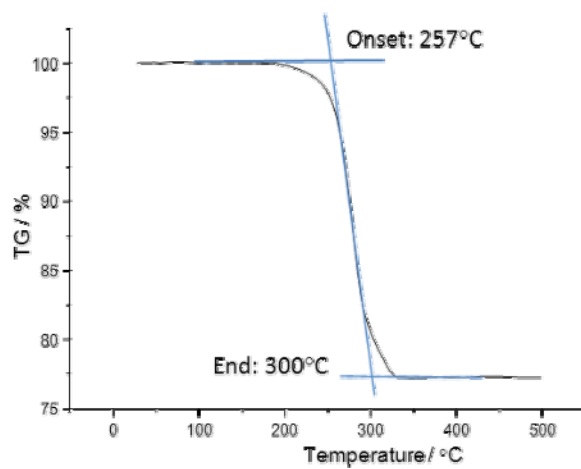
**Figure S6.** Powder X-ray diffraction pattern for the residue after TGA ( $T = 25\text{-}500^\circ\text{C}$ ) of compound **1**, identified as  $\text{SnSe}_2$ .



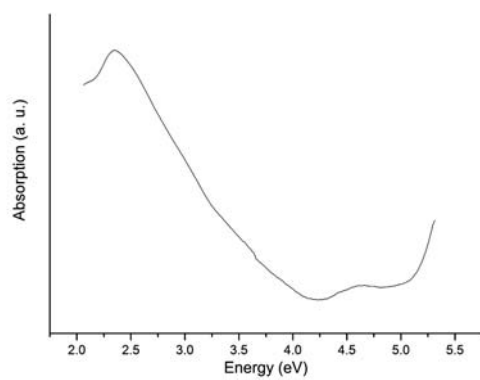
**Figure S7.** Powder X-ray diffraction pattern for the residue after TGA ( $T = 25\text{-}800^{\circ}\text{C}$ ) of compound **1**, identified as SnSe.



**Figure S8.** TGA diagram for compound **1** in the temperature range  $25\text{-}800^{\circ}\text{C}$ .



**Figure S9.** TGA diagram for compound **1** in the temperature range  $25\text{-}500^{\circ}\text{C}$ .



**Figure S10.** UV-visible spectrum of compound 1 in the solid state.