Electronic Supplementary Material (ESI) for Chemical Communications

From Selenidostannates to Silver-Selenidostannate: Structural Variation of Chalcogenidometallates Synthesized in Ionic Liquids

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Supporting Information

1. X-ray crystallography

The intensity data were collected on a Rigaku SCXmini CCD diffractometer for **1**, a Rigaku Mercury CCD diffractometer for **2**, and **4**, an Oxford Diffraction Xcalibur Eos diffractometer for **3** and **6** at room temperature, and an Oxford Diffraction Supernova diffractometer for **5** at 100K with graphite-monochromated Mo$K\alpha$ radiation (□λ □= 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97[1] program package. The C and N atoms in compounds **1**-**6** were located from difference-Fourier maps and refined with restraints (DFIX, SADI, FLAT, ISOR and SIMU) to obtain chemical-reasonable models for imidazolium ions, and the hydrogen atoms attached to the C and N atoms were located at geometrically calculated positions.

Reference

[1] G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of Göttingen, Germany, **1997**.

Talbe S1 The crystallographic data for compound **1**, **2**, **3**, **4** ,**5** and **6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{32}H_{60}N_8Se_{20}Sn_9$	$C_{16}H_{30}N_4Se_7Sn_3$	$C_{16}H_{30}N_4Se_7Sn_3$	$C_{18}H_{34}N_4Se_7Sn_3$	$C_{18}H_{34}N_4Se_7Sn_3$	$C_{63}H_{119}N_{14}AgSe_{28}Sn_{12}$
Crystal Size (mm)	0.31×0.20×0.15	0.21 x 0.20 x 0.15	0.21 x 0.20 x 0.11	0.28 x 0.18 x 0.14	0.15×0.12×0.11	0.33×0.15×0.08
Crystal system	Monoclinic	monoclinic	trigonal	monoclinic	trigonal	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P3_221$	$P2_1/c$	$P3_221$	P-1
a (Å)	18.652(6)	14.270(5)	13.9470(3)	24.538(4)	13.9381(4)	10.8983(4)
b (Å)	20.353(6)	15.549(6)	13.9470(3)	13.961(2)	13.9381(4)	13.5554(6)
c (Å)	20.196(6)	14.377(5)	27.8553(8)	19.434(4)	27.7737(12)	23.0906(10)
α (°)	90	90	90	90	90	88.904(3)
β (°)	105.244(6)	92.749(7)	90	94.539(3)	90	86.700(3)
γ (°)	90	90	120	90	120	68.230(4)
V (Å^3)	7397(4)	3186(2)	4692.5(2)	6637(2)	4672.7(3)	3162.6(2)
Z	4	4	6	8	6	1
μ (mm^{-1})	12.856	10.342	10.534	9.933	10.581	10.568
λ(MoKα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	5752	2168	3252	4464	3348	2164
θ range (°)	2.30 to 27.49	2.36 to 27.49	2.77 to 25.35	2.21to 27.49	2.92 to 26.35	2.29 to 26.00
Reflections	57208	24428	10635	50421	18626	21587
Independent	16902	7259	5613	15171	6280	12155
Observed Reflection [$I>2\sigma(I)$]	12076	5697	4159	12041	4987	8734
Temperature	293	293	293	293	173	293
ρ_{calc}/g cm^{-3}	2.877	2.475	2.521	2.432	2.591	2.528
Flack Parameter			0.010 (19)		0.156 (19)	
Parameter	690	277	353	721	386	896
R_{int}	0.0654	0.0448	0.0412	0.0373	0.0501	0.0280
R_1, wR_2	0.0594, 0.1359	0.0481, 0.1075	0.0519, 0.1099	0.0443, 0.1095	0.0557, 0.1531	0.0438, 0.0884
R_1 , wR_2 [all data]	0.0884, 0.1523	0.0661, 0.1190	0.0826, 0.1262	0.0597, 0.1196	0.0761, 0.1698	0.0744, 0.1017
GOF	1.077	1.056	1.069	1.091	1.060	1.011
Largest diff. Peak and hole/e Å^{-3}	1.169, -1.667	0.960, -1.341	1.140, -1.271	1.212, -1.233	1.488, -1.838	0.918, -0.841

[a] $R1 = \sum||Fo|-|Fc||/\sum|Fo|$, $wR2 = \{\sum w[(Fo)^2-(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$

2. More Structural details

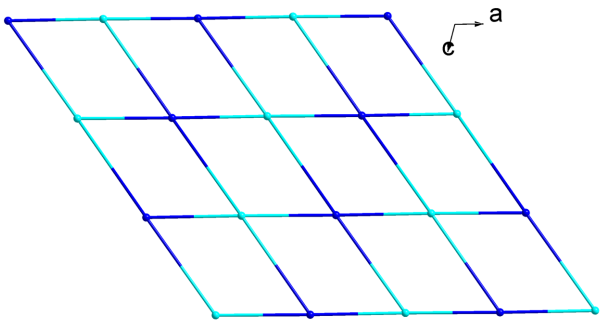


Fig. S1 a) Schematic view of the $(4^4{\cdot}4^4)$ net in **1** along the *b* axis; the $[Sn_6Se_{10}]$ and $[Sn_3Se_{10}]$ function as 4-connected nodes.

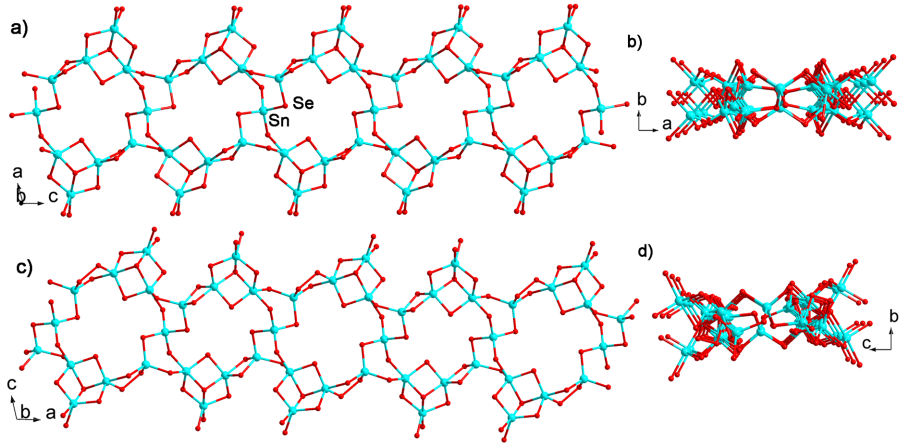
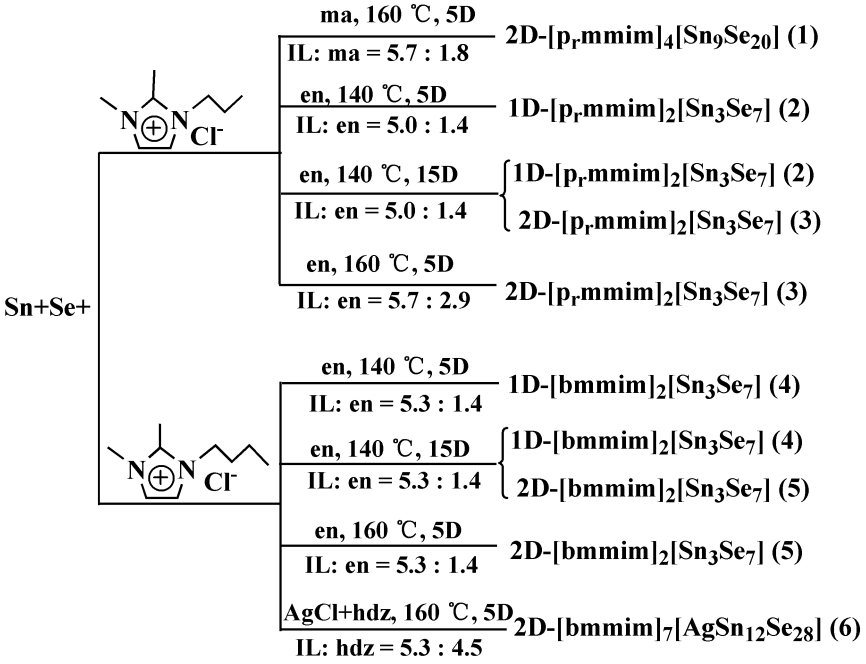


Fig. S2 a) View of the double-chain in **1** extended along the *b*-axis. Alternatively, the structure of **1** can be described as the $[SnSe_4]$ tetrahedra connecting one $[Sn_3Se_4]$ semicube by corner-bridging and another $[Sn_3Se_4]$ semicube by edge-bridging to form an infinite chain. Then two such chains are linked by $[SnSe_4]$ tetrahedra via corner-bridging to form a $[Sn_9Se_{19}]$ double-chain. Each double-chain further connects two adjacent double-chains by edge-bridging the $[Sn_3Se_4]$ semicubes through two Se atoms, resulting in a 2D network along the *ac* plane. b) View of the double-chain in **1** running along the *c*-axis. c) View of the double-chain in 3D-$[bmmim]_4[Sn_9Se_{19}(Se_2)_{0.9}Se_{0.1}]$ extended along the *b*-axis. d) View of the double-chain in 3D-$[bmmim]_4[Sn_9Se_{19}(Se_2)_{0.9}Se_{0.1}]$ running along the *a*-axis. The $[Sn_9Se_{19}]$ double-chain in **1** is close related to that in 3D-$[bmmim]_4[Sn_9Se_{19}(Se_2)_{0.9}Se_{0.1}]$ and 3D-$[pmmim]_4[Sn_9Se_{19}(Se_2)_{0.93}Se_{0.07}]$,[1] ignoring the difference between $[SnSe_4]$ and $[SnSe_3(Se)_2]$. The double-chain of compound **1** connects two adjacent double-chains leading to a 2-D network, whereas the counterparts of 3D-$[bmmim]_4[Sn_9Se_{19}(Se_2)_{0.9}Se_{0.1}]$ and 3D-$[pmmim]_4[Sn_9Se_{19}(Se_2)_{0.93}Se_{0.07}]$ link four adjacent double-chains to form the 3D networks.

[1] J. R. Li, Z. L. Xie, X. W. He, L. H. Li, X. Y. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 11395.

3. Synthesis



Scheme S1. Typical crystallization processes of new selenidostannates or silver-selenidostannate in mixed solvents of ionic liquids and a small amount of amines (ma = methylamine (33% aq.); en = ethylenediamine; hdz = hydrazine hydrate).

3a). Synthesis of **1:** A mixture of Sn (1.0 mmol, 0.119 g), selenium (2.5 mmol, 0.197 g), [$p_r$mmim]Cl (1-propyl-2, 3-dimethyl-imidazolium chloride, 5.7 mmol, 1.0 g) and methylamine (1.8 mmol, 0.170 g, 33% aq.) was sealed in a 20-mL teflon-lined bomb and was kept at 160 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, then the orange rod-like crystals of **1** were obtained by filtration and air-dried (Yield: 0.185 g, 52% based on Sn).

3b). Synthesis of **2:** A mixture of Sn (1.0 mmol, 0.119 g), selenium (2.5 mmol, 0.197 g), [$p_r$mmim]Cl (5.0 mmol, 0.85 g) and ethylenediamine (1.4 mmol, 0.090 g) was sealed in a 20-mL teflon-lined bomb and was kept at 160 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, then the orange-red brick-like crystals of **2** were obtained by filtration and air-dried (Yield: 0.206 g, 50% based on Sn).

3c). Synthesis of **3:** A mixture of Sn (1.0 mmol, 0.119 g), selenium (2.5 mmol, 0.197 g), [$p_r$mmim]Cl (5.0 mmol, 0.85 g) and ethylenediamine (2.9 mmol, 0.180 g) was sealed in a 20-mL teflon-lined bomb and was kept at 160 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, then the red lathe crystals of **3** were obtained by filtration and air-dried (Yield: 0.116 g, 28% based on Sn).

3d). Synthesis of **4:** A mixture of Sn (1.0 mmol, 0.119 g), selenium (2.5 mmol, 0.197 g), [bmmim]Cl (5.3 mmol 1-butyl-2,3-dimethyl-imidazolium chloride, 1.0 g) and ethylenediamine (1.4 mmol, 0.090 g) was sealed in a 20-mL teflon-lined bomb and was kept at 140 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, then the red block-like crystals of **3** were obtained by filtration and air-dried (Yield: 0.129 g, 32% based on Sn).

3e). Synthesis of **5:** A mixture of Sn (1.0 mmol, 0.119 g), selenium (2.5 mmol, 0.197 g), [bmmim]Cl (5.3 mmol, 1.0 g) and ethylenediamine (1.4mmol, 0.090 g) was sealed in a 20-mL teflon-lined bomb and was kept at 160 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, then the red polyhedron-like crystals of **5** were obtained by filtration and air-dried (Yield: 0.175 g, 43% based on Sn).

3f). Synthesis of **6:** A mixture of Sn (0.5 mmol, 0.060 g), selenium (1.4 mmol, 0.114 g), AgCl (0.33 mmol, 0.047 g) [bmmim]Cl (5.3 mmol 1.0 g) and hydrazine monohydrate (5.2mmol, 2.69 g) was sealed in a 20-mL teflon-lined bomb and was kept at 160 ^{o}C for five days, which was then slowly cooled to room temperature. The product was washed with water and ethanol, and then the red brick-like crystals of **6** accompanied by black powder of Ag_8SnSe_6 were obtained by filtration and air-dried. The red crystal can be separated by hand (Yield: 0.026 g, 13% based on Sn).

4. Physical measurements

All chemicals employed in this study were analytical reagents and commercially available without further purification. N, C and H analyses were performed on a German Elementary Vario EL III instrument. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex Ⅱ using Cu$K\alpha$ radiation. Optical diffuse reflectance spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectra by using the Kubelka–Munk function: $a/S=(1-R)^2/2R$,[1] where a is the absorption coefficient, S is the scattering coefficient which is practically independent of wavelength when the particle size is larger than 5 μm, and R is the reflectance. Thermogravimetric analyses were carried out with a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min under a nitrogen atmosphere.

[1] Wendlandt, W. M.; Hecht, H. G. *Reflectance Spectroscopy*, Interscience, New York, **1966**.

4a). Elemental analyses

Table S2. Elemental analyses of **1**, **2**, **3**, **4** and **5**.

Compound	Empirical formula	Experiment (%)			Calculated (%)		
		N	C	H	N	C	H
1	$C_{32}H_{60}N_8Se_{20}Sn_9$	3.57	12.20	2.03	3.50	11.99	1.89
2	$C_{16}H_{30}N_4Se_7Sn_3$	4.65	16.11	2.45	4.72	16.19	2.55
4	$C_{18}H_{34}N_4Se_7Sn_3$	4.15	16.92	2.59	4.61	17.79	2.82
5	$C_{18}H_{34}N_4Se_7Sn_3$	4.64	17.13	2.60	4.61	17.79	2.82
6	$C_{63}H_{119}N_{14}AgSe_{28}Sn_{12}$	4.08	15.92	2.77	4.07	15.71	2.49

4b). PXRD

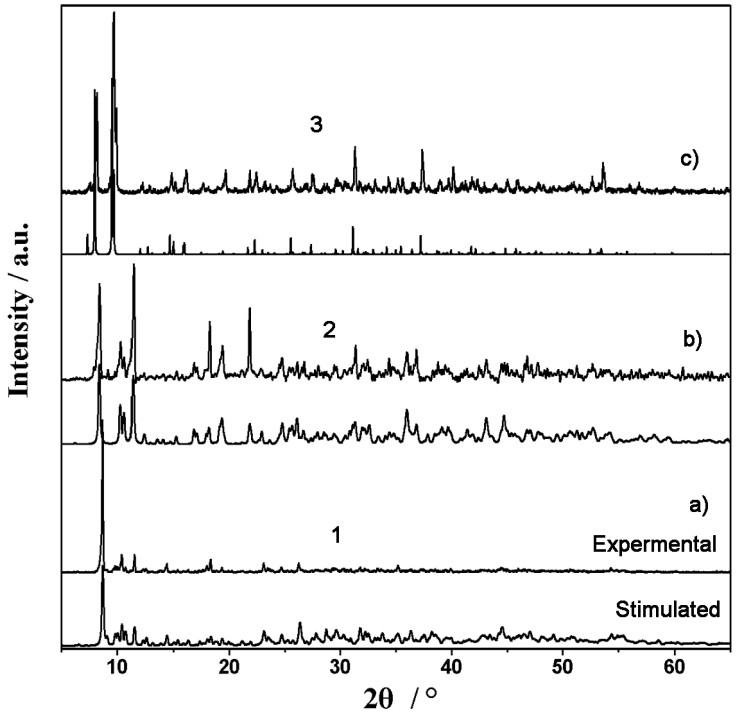


Fig. S3 The PXRD patterns of compounds **1**, **2** and **3** (top) are comparable with those simulated from the single crystal X-ray data (bottom), respectively.

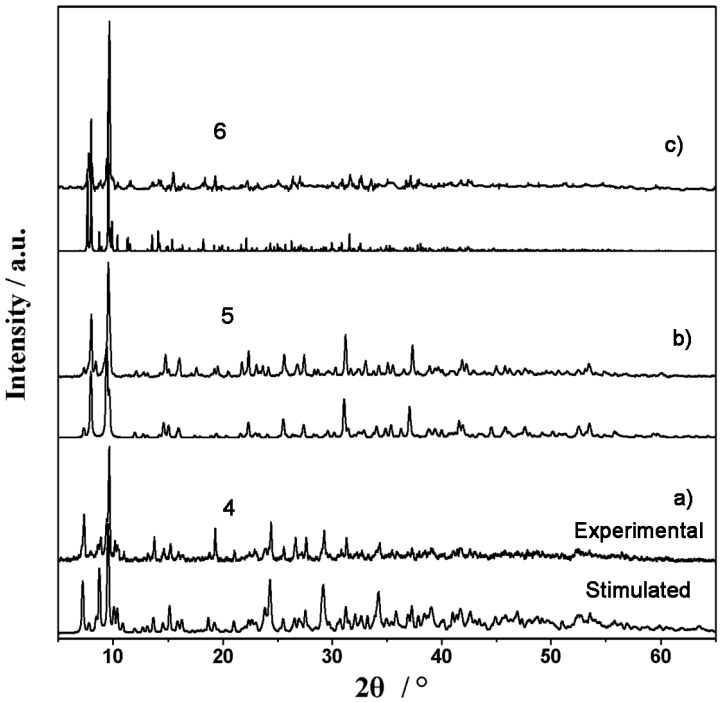


Fig. S4 The PXRD patterns of the compounds **4**, **5** and **6** (top) are comparable with those simulated from the single crystal X-ray data.

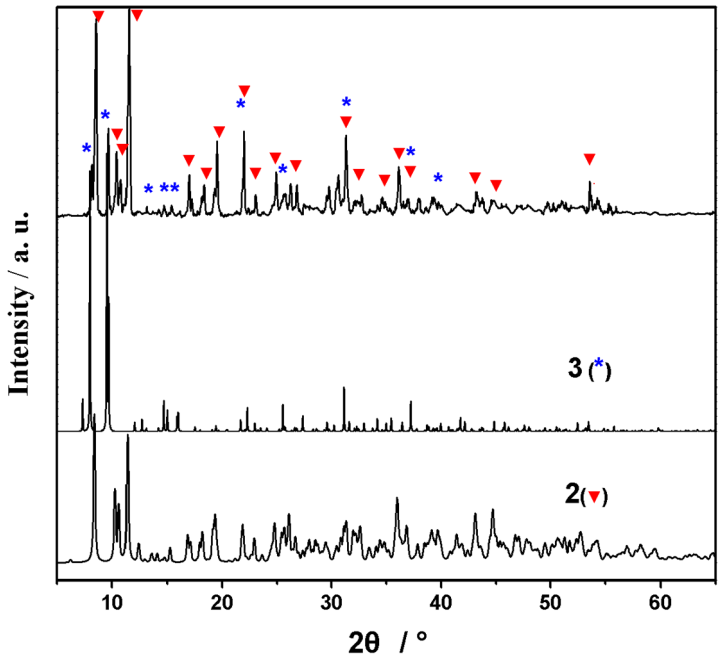


Fig. S5 Top**:** the PXRD patterns of the products obtained from the reactions of tin, selenium, [$p_r$mmim]Cl and ethylenediamine in a molar ratio of 1:2.5:5.0:1.4 at 140 ^{o}C for 15 days. Bottom: the PXRD patterns of the single-phased compounds **2** and **3**.

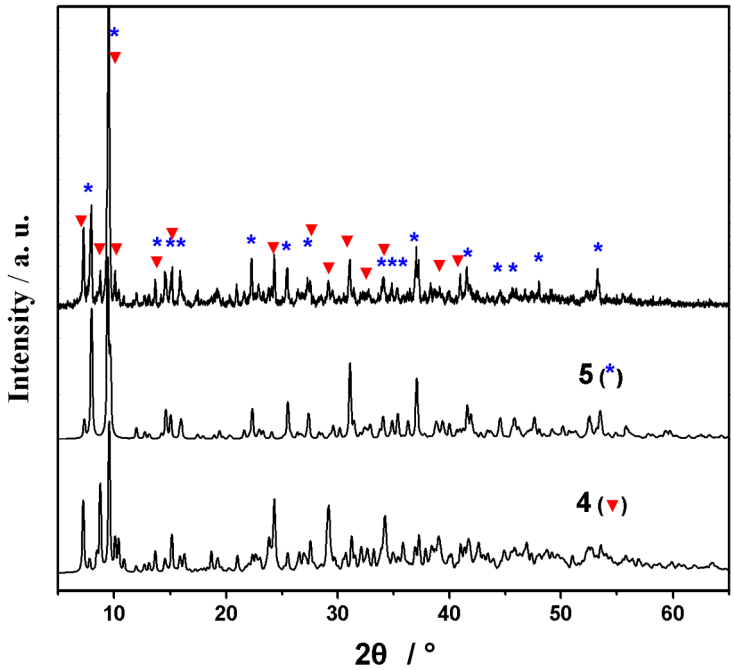


Fig. S6 Top**:** the PXRD patterns of the products obtained from the reactions of tin, selenium, [bmmim]Cl and ethylenediamine in a molar ratio of 1:2.5:5.3:1.4 at 140 ^{o}C for 15 days. Bottom: the PXRD patterns of the single-phased compounds **4** and **5**.

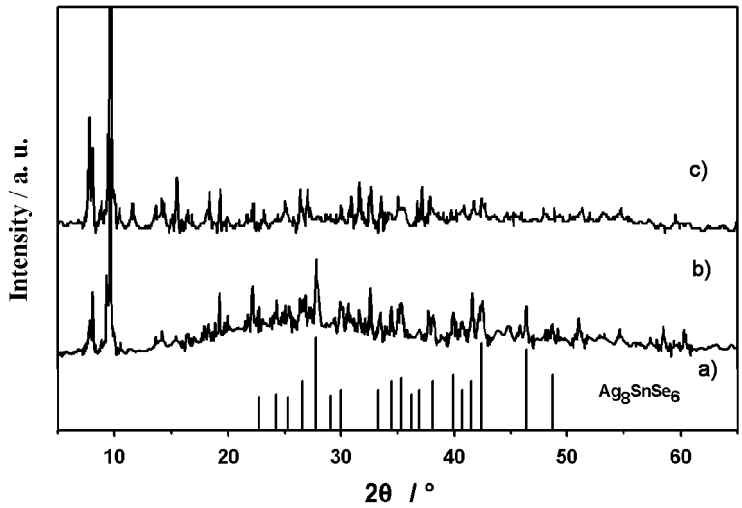


Fig. S7 The PXRD pattern (b) of the products obtained from the reaction of tin, selenium, silver chloride, [bmmim]Cl and ethylenediamine in a molar ratio of 1:2.8:0.66:10.6:10.2 at 160 °C for 5 days is identified as the mixture of **5** (c) and Ag_8SnSe_6 (a).

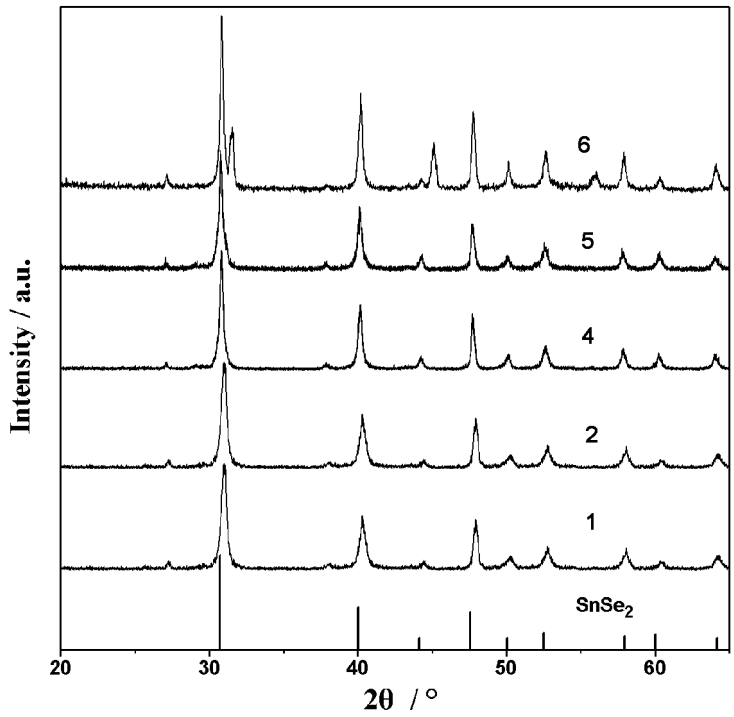


Fig. S8 The PXRD patterns for the post-TGA residues of compounds **1**, **2**, **4**, **5** and **6**. The theoretical X-ray diffraction pattern of $SnSe_2$ is shown at bottom for comparison. The residues of compounds **1**, **2**, **4** and **5** are identified as pure phase of $SnSe_2$, while that of **6** is identified as the mixture of $SnSe_2$ as major phase and a minor unknown phase.

4d). TGA

The thermal stabilities of **1**, **2**, **4**, **5** and **6** were investigated on pure samples in a N_2 atmosphere from ~25 to 450℃. As shown in Fig. S7, the TGA curves of these compounds displayed two or three steps of weight losses from ~230-370℃. All the weight losses are in correspondence with the losses of organic components and H_2Se molecules. The post-TGA residues of **1**, **2**, **4**, **5** were identified as $SnSe_2$, and that of **6** is identified as the mixture of $SnSe_2$ as major phase and a minor unknown phase (Fig. S9) by PXRD.

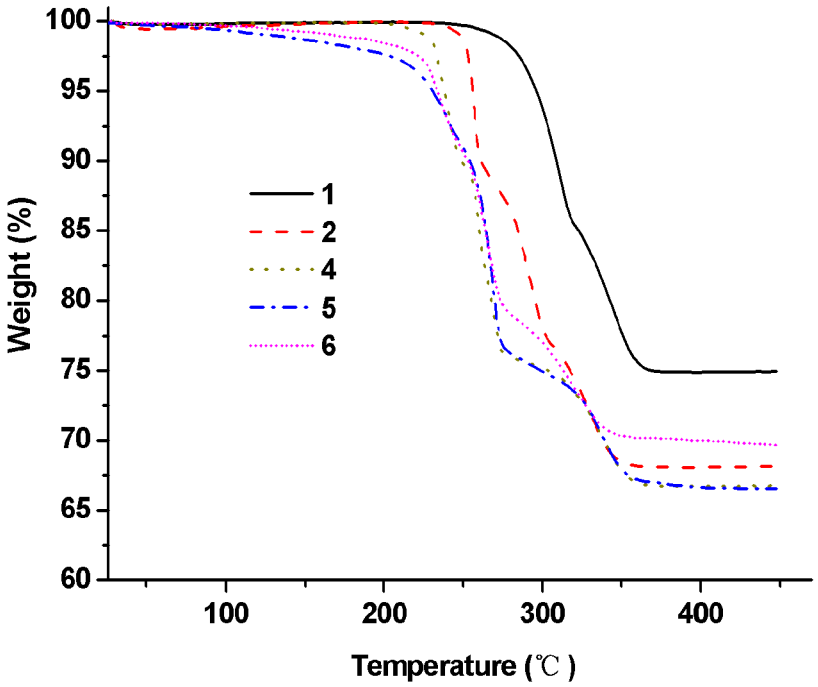


Fig. S9. TGA curves of compounds **1**, **2**, **3**, **4** and **5**.

Table S3. Detailed reports of the TGA data of **1**, **2**, **3**, **4** and **5**.

Compound	Empirical formula	Calculated weight loss %	Experimental weight loss %
1	$C_{32}H_{60}N_8Se_{20}Sn_9$	22.3	24.7
2	$C_{16}H_{30}N_4Sn_3Se_7$	33.3	31.5
4	$C_{18}H_{34}N_4Sn_3Se_7$	34.7	33.1
5	$C_{18}H_{34}N_4Sn_3Se_7$	34.7	33.2
6	$C_{63}H_{119}N_{14}AgSe_{28}Sn_{12}$	28.0	29.4