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Assembly and structural transformation of organic-decorated manganese selenidostannates

Cheng–Feng Du,[a,b] Mei–Ling Feng,[a] Jian–Rong Li,[a] Guo–Dong Zou,[a,b] Ke–Zhao Du,[a] and Xiao–Ying Huang*[a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. Fax: (+86) 591-83793727

[b] University of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China.

E-mail: xyhuang@fjirsm.ac.cn

Supporting Information

1. Synthesis

1a). Synthesis of **1:** The synthesis of **1** was carried out by a simple hydrothermal method. In a typical reaction, 0.198g (1 mmol) $MnCl_2 \cdot 4H_2O$, 0.267g (1 mmol) $Na_2SnO_3 \cdot 3H_2O$ and 0.198g (2.5 mmol) Se powder was mixed and dispersed in 5 mL glycerol, 1 mL (15 mmol) en was added, the mixture was transferred to a 20 mL Teflon-lined steel autoclave and kept at 160 °C for 8 days. After it cooled to room temperature, the product was washed with ethanol, then the bright red block crystals of **1** were obtained (Yield: 0.401 g, 75.94% based on Sn).

1b). Synthesis of **2:** 0.198g (1 mmol) $MnCl_2 \cdot 4H_2O$, 0.267g (1 mmol) $Na_2SnO_3 \cdot 3H_2O$ and 0.198g (2.5 mmol) Se powder was mixed and dispersed in 5 mL glycerol, 0.5 mL (7.5 mmol) en was added, the mixture was transferred to a 20 mL Teflon-lined steel autoclave and kept at 160 °C for 8 days. After it cooled to room temperature, the product was washed with ethanol, then the red needle-liked crystals of **2** were obtained (Yield: 0.166 g, 35.46% based on Sn).

1c). Synthesis of **3:** 0.198g (1 mmol) $MnCl_2 \cdot 4H_2O$, 0.267g (1 mmol) $Na_2SnO_3 \cdot 3H_2O$ and 0.316g (4 mmol) Se powder was mixed and dispersed in 4 mL glycerol, 0.75 mL (11.25 mmol) en was added, the mixture was transferred to a 20 mL Teflon-lined steel autoclave and kept at 160 °C for 8 days. After it cooled to room temperature, the product was washed with ethanol, then the tawny block crystals of **3** were obtained (Yield: 0.286 g, 43.25% based on Sn).

1e). Structural transformation experiments for compound **1** to **2:** 5 mg crystals of **1** were grind and heat to different temperature (150 ~ 250 °C) at a heating rate of 5 °C/min, then kept at the temperature for 1h. The experiments were carried out with a NETZSCH STA 449F3 unit under a nitrogen atmosphere.

1f). Structural transformation experiment for compound **2** to **1:** 0.086 g crystals of **2**, 0.8 mL en and 4 mL glycerol was mixed and the mixture was transferred to a 20 mL Teflon-lined steel autoclave and kept at 160 °C for 6 days. After cooled to room temperature, the product was washed with ethanol.

2. X-ray crystallography

The intensity data were collected on a Oxford Diffraction Xcalibur Eos diffractometer for **1**, **2** and **3** at room temperature with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX2013[1] program package. The C and N atoms in the en of compound **2** are highly disordered with two split positions and were refined with restraints (DFIX, SADI, DELU and SIMU) to obtain chemical-reasonable models for en molecule. The crystal data and details of refinements of compounds **1** to **3** are depicted in Table S1.

Reference

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

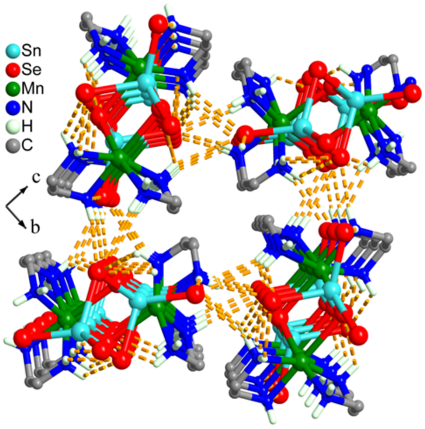

Figure S1. Interconnection of the chains via the N─H···S hydrogen bonds (dashed lines) results in a 3D supramolecular structure in compound **1**. H atoms of CH_2 are omitted for clarity.

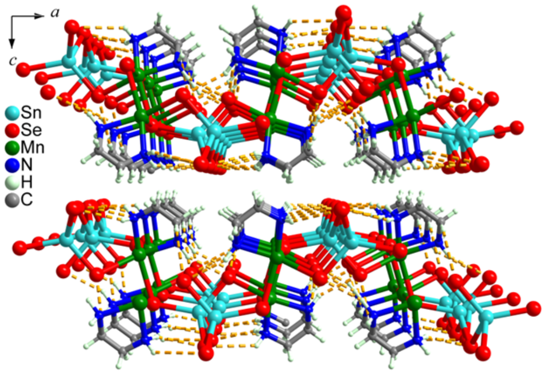

Figure S2. View of stacking of the layers in **2** along the *b*-axis.

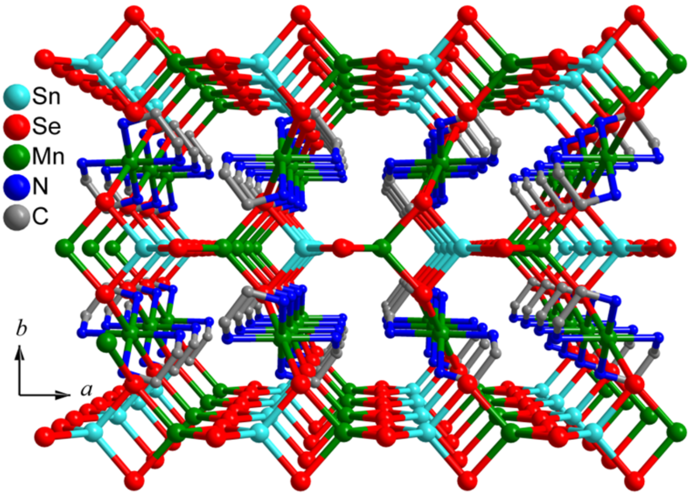

Figure S3. Perspective view of the 3D network of **3** along the *c* axis. H atoms are omitted for clarity.

Talbe S1. The crystallographic data for compounds **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Formula	$C_4H_{16}MnN_4Se_3Sn$	$C_2H_8MnN_2Se_3Sn$	$C_4H_{16}Mn_2N_4Se_4Sn$
M_r (g mol^{-1})	530.72	470.61	664.62
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	*Pbca*	*Pnma*
D_{calcd} (g cm^{-3})	2.657	3.097	2.858
a (Å)	9.4565(4)	13.9290(5)	13.1101(4)
b (Å)	11.2896(4)	7.5261(2)	14.8267(6)
c (Å)	12.7937(5)	19.2572(9)	7.9466(2)
α (°)	90	90	90
β (°)	103.765(4)	90	90
γ (°)	90	90	90
V (Å^3)	1326.63(9)	2018.75(13)	1544.66(9)
Z	4	8	4
μ (mm^{-1})	11.034	14.475	12.618
R_{int}	0.0274	0.0329	0.0198
Params/restraints/data	118/0/2805	119/194/2130	76/0/1641
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0291	0.0478	0.0234
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.0555	0.1338	0.0538
Goodness of fit	1.008	1.046	1.041

^{a} $R_1=\sum(F_o - F_c)/\sum F_o$. ^{b} $wR_2=[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

3. 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*Kα* 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: $a/S = (1\text{-}R)^2/2R$,[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 10 °C/min under a nitrogen atmosphere.

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

3a). PXRD

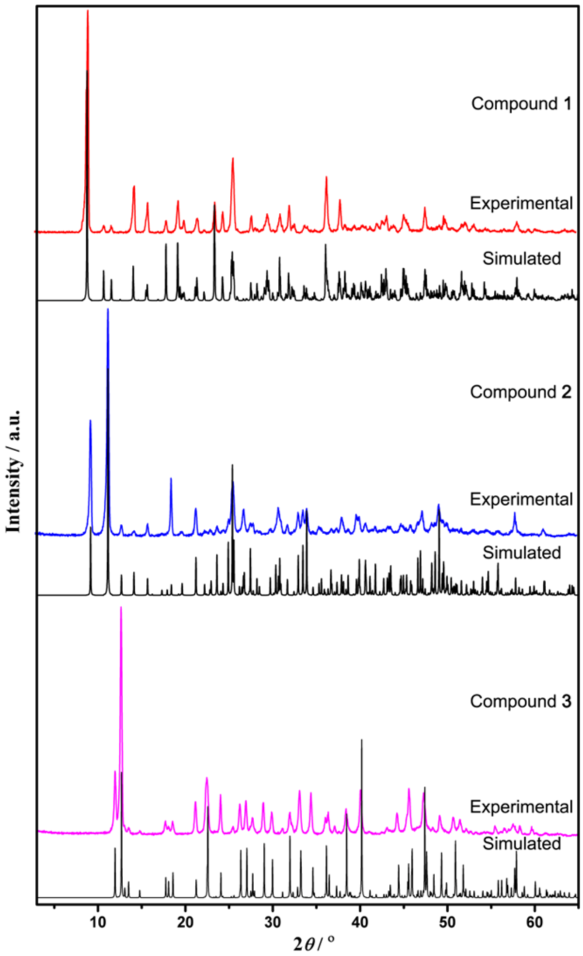

Figure S4. The PXRD patterns of compounds **1**, **2** and **3** (top) are comparable with those simulated from the single crystal X-ray data (bottom), respectively.

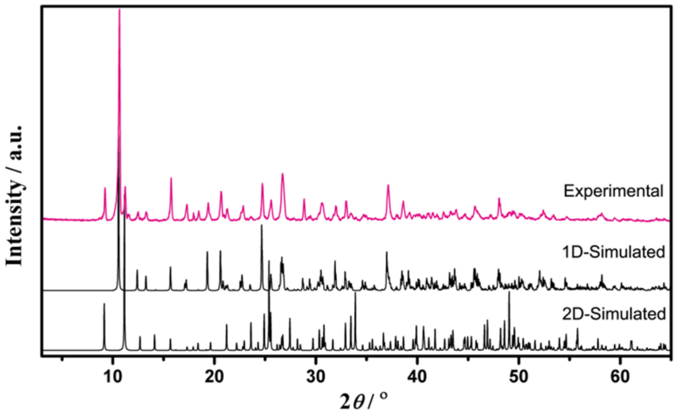

Figure S5. The PXRD patterns of crystal transformation experiment from compound **2** to **1** (top) are comparable with those simulated from the single crystal X-ray data (bottom), respectively. The sample was obtain as the mixture after reaction without further seperation.

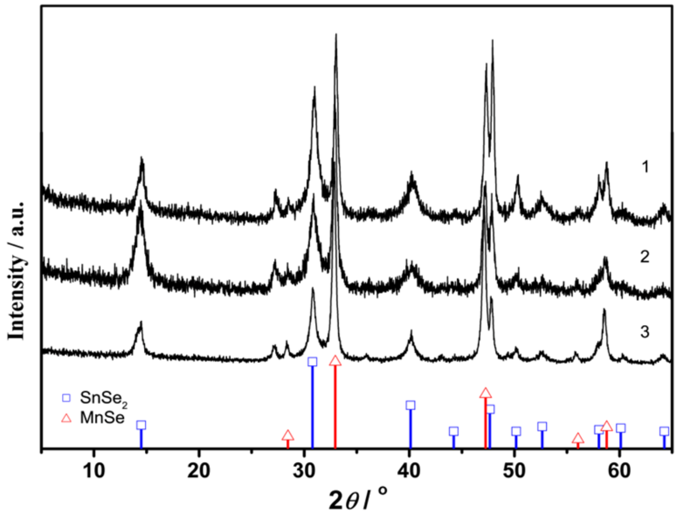

Figure S6. The PXRD patterns for the post-TGA residues of compounds **1**, **2** and **3**. The theoretical X-ray diffraction pattern of $SnSe_2$ and MnSe are shown at bottom for comparison. The residues of compounds **1**, **2** and **3** are identified as the mixture of $SnSe_2$ and MnSe phase.

3b). Elemental analyses

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

Compound	Empirical formula	Experiment (%)			Calculated (%)		
		N	C	H	N	C	H
1	$C_4H_{16}MnN_4Se_3Sn$	10.78	9.28	3.26	10.56	9.04	3.01
2	$C_2H_8MnN_2Se_3Sn$	5.89	5.43	1.92	5.95	5.10	1.70
3	$C_4H_{16}Mn_2N_4Se_4Sn$	8.37	7.22	2.42	8.42	7.22	2.41

3c). TGA

The thermal stabilities of **1**, **2** and **3** were investigated on pure samples at a heating rate of 10 °C/min in a N_2 atmosphere from 30 to 500 °C. As shown in Figure S7, the TGA curves of these compounds displayed one or two steps of weight losses from 250~350 °C, which are in correspondence with the losses of organic components (*en* molecules). The post-TGA residues of **1**, **2**, **3** were identified as the mixture of $SnSe_2$ and MnSe phase (Figure S7) by PXRD.

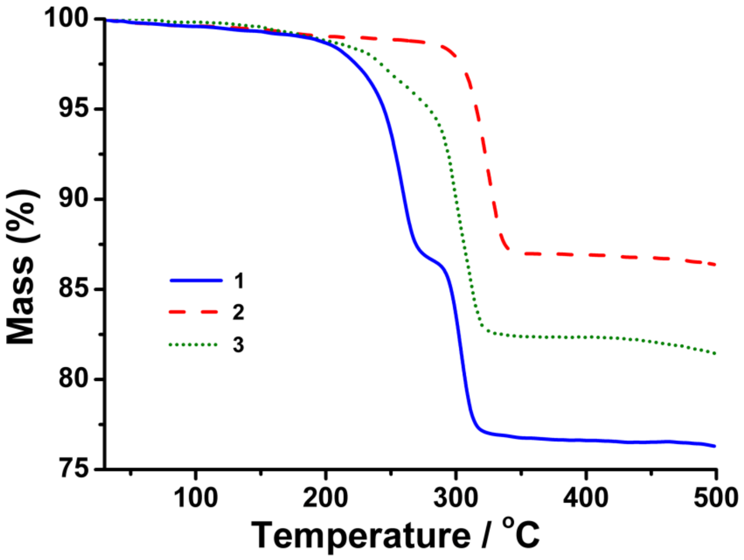

Figure S7. TGA curves of compounds **1**, **2** and **3**.

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

Compound	Empirical formula	Calculated weight loss at 400 °C (%)	Experimental weight loss at 400 °C (%)
1	$C_4H_{16}MnN_4Se_3Sn$	22.7	23.4
2	$C_2H_8MnN_2Se_3Sn$	12.8	13.1
3	$C_4H_{16}Mn_2N_4Se_4Sn$	18.1	18.5

3d). EDX spectra

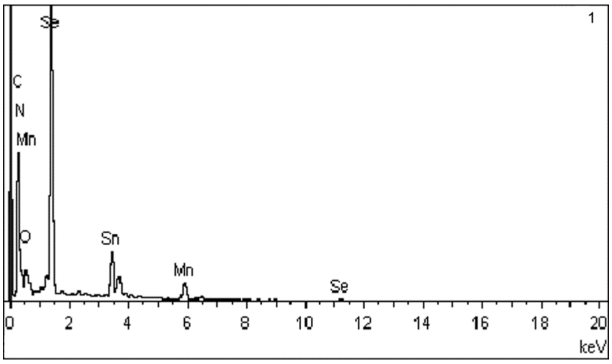

Figure S8. EDX spectra of compound **1**.

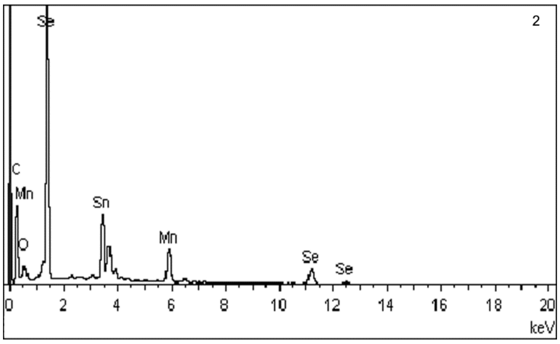

Figure S9. EDX spectra of compound **2**.

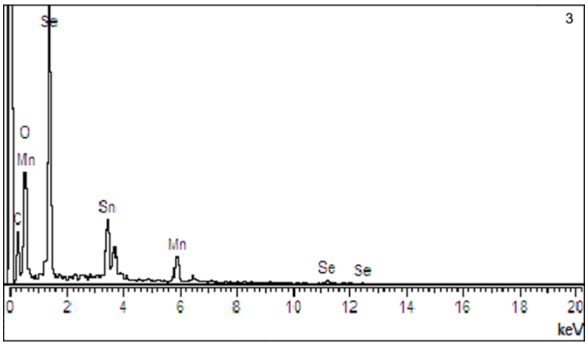

Figure S10. EDX spectra of compound **3**.

4. Theoretical calculation

The band structures, density of states (DOS) and partial density of states (PDOS) of compounds **1**, **2** and **3** were calculated based on the DFT method using the computer code CASTEP (Figures S11, S12, and S13). The band structures along high symmetry points of the first Brillouin zone were calculated. It is found that **1** and **2** have the direct band gap of 1.49 eV and 1.07 eV, respectively. While **3** has the indirect band gap of 1.64 eV.

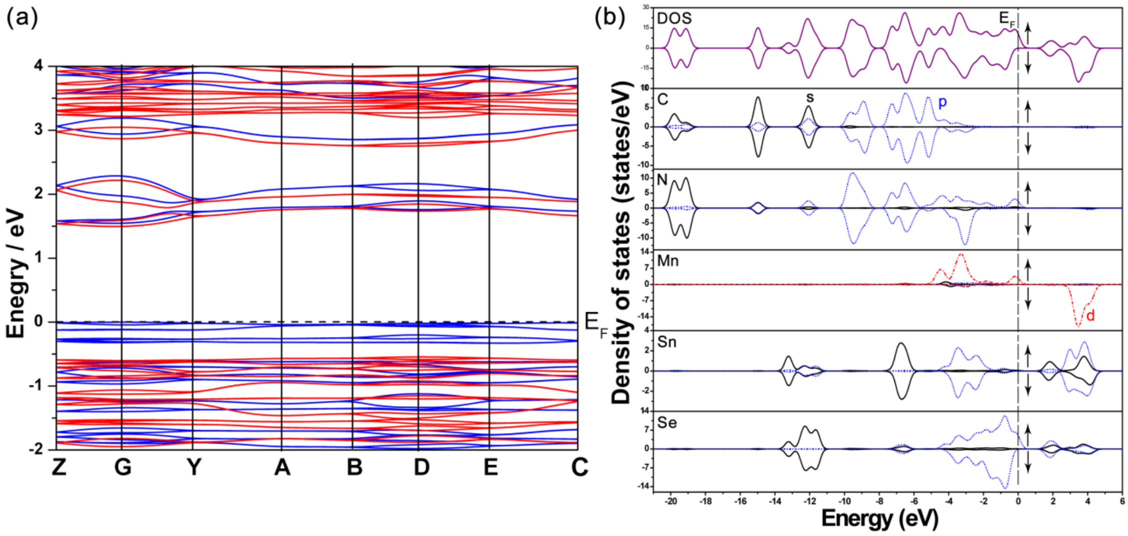

Figure S11. (a) The band structure of **1**. Fermi level is set at 0 eV (dot line); (b) partial density of states calculation and density-of-states analysis for **1**.

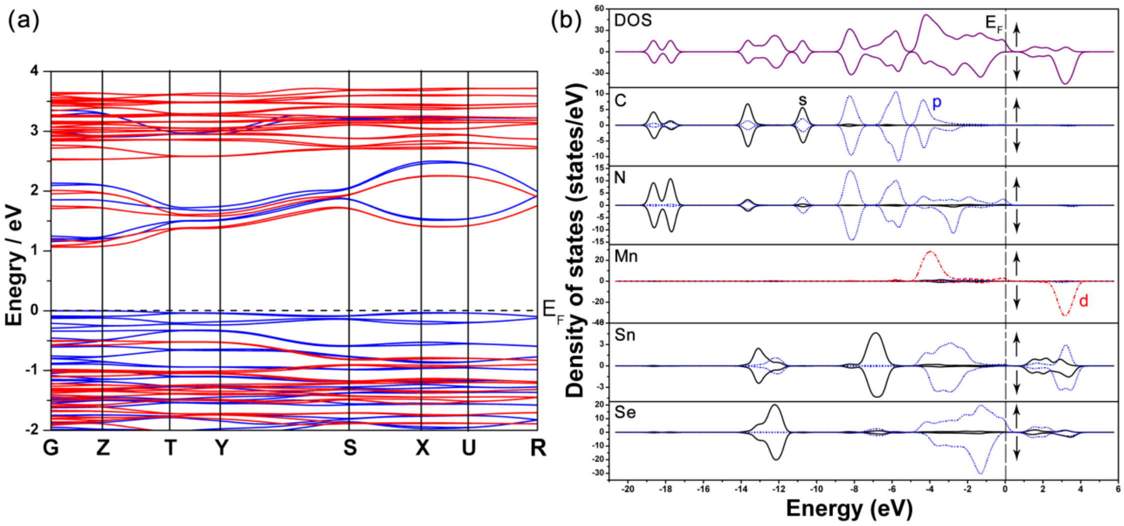

Figure S12. (a) The band structure of **2**. Fermi level is set at 0 eV (dot line); (b) partial density of states calculation and density-of-states analysis for **2**.

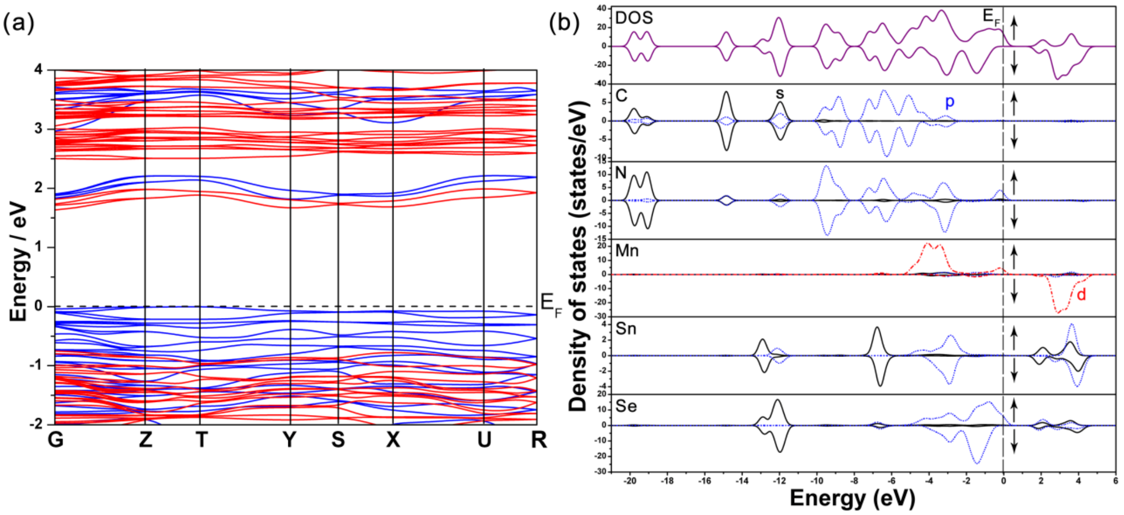

Figure S13. (a) The band structure of **3**. Fermi level is set at 0 eV (dot line); (b) partial density of states calculation and density-of-states analysis for **3**.