

Supporting Information

A hybrid linkage mode between T2,2 and T3 selenide clusters

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1. Single-crystal structure determination

Intensity data collections were carried out with the Bruker APEX-II diffractometer and equipped with a CCD two-dimensional detector using the graphite monochromatized wavelength $\lambda(\text{Mo-}K\alpha)=0.71073 \text{ \AA}$ at 296(2) K. The structure was solved with direct methods using *SHELXS-97* [1], and structure refinement was performed by full matrix least-squares on F^2 using the *SHELXL-97* crystallographic software package [2]. All atoms except those in disordered extra-framework species inside large cavities were determined and refined with anisotropic displacement parameters. Such an observation is similar to that found for open framework selenides. [3] The disorder of amine molecules in selenides is apparently due to the weak host–guest interaction. In particular, the N–H...Se type hydrogen bonding is considerably weaker than the N–H...O type that is often responsible for the ordering of guest amine molecules in oxides. Relevant crystallographic data and refinement details for open framework of compound **1** are summarized in Table S1. Selected bond lengths and angles are listed in Table S2 and Table S3, respectively.

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Response:

During the structure analysis, it was found that the unit cell possesses large voids. Disordered extra-framework species (template and water molecules) inside large cavities could not be determined as well-defined atoms in the difference electron density map.

Table S1. Crystallographic data of **1** based on GeInSe-PPZ framework.

Anion formula	$[\text{Ge}_{3.88}\text{In}_{22.12}\text{Se}_{50}]^{18.12-}$
Formula weight	6785.47
Temperature (K)	296 (2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	<i>I4(1)/a</i>
<i>a</i> (Å)	22.4956(10)
<i>b</i> (Å)	22.4956(10)

c (Å)	37.984(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	19222(2)
Z	4
D_c (g cm ⁻³)	2.345
μ (mm ⁻¹)	12.667
$F(000)$	11664
θ range (°)	1.67, 24.39
hkl range	-25,25; -24, 25; -44, 44
Reflections	52257
Data/restraints/parameters	7813/0/175
R_{int}	0.1378
GOF	1.043
$R_1, \omega R_2 [I > 2\sigma(I)]$ ^[a]	0.0691, 0.2078
$R_1, \omega R_2$ (all data) ^[a]	0.1548, 0.2609
Largest diff. peak and hole (e Å ⁻³)	2.237, -0.919

$$^{[a]} R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \omega R_2 = \{ \Sigma [\omega(F_o^2 - F_c^2)^2] / \Sigma [\omega(F_o^2)^2] \}^{1/2}$$

Table S2. Selected bond lengths (Å) for compound **1^a**.

In(1)-Se(1)	2.523(3)	In(1)-Se(1)#1	2.523(3)
In(1)-Se(2)	2.622(2)	In(1)-Se(2)#1	2.622(2)
In(2)-Se(2)	2.611(3)	In(2)-Se(2)#2	2.615(3)
In(2)-Se(3)	2.519(3)	In(2)-Se(4)	2.539(3)
In(3)-Se(1)#1	2.553(3)	In(3)-Se(3)#2	2.575(3)
In(3)-Se(4)	2.571(3)	In(3)-Se(5)	2.560(3)
In(4)-Se(5)	2.529(3)	In(4)-Se(6)	2.552(3)
In(4)-Se(7)	2.555(3)	In(4)-Se(8)	2.548(3)
In(5)-Se(6)	2.505(3)	In(5)-Se(9)	2.501(3)
In(5)-Se(10)	2.512(3)	In(5)-Se(13)	2.498(3)
In(6)-Se(8)	2.493(3)	In(6)-Se(11)	2.486(3)
In(6)-Se(12)	2.489(3)	In(6)-Se(13)	2.466(3)
In(7)-Se(7)	2.453(3)	In(7)-Se(10)	2.468(3)

In(7)-Se(11)	2.452(3)	In(7)-Se(12)#3	2.466(3)
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^a Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1/2,z+0, #2 y+3/4,-x+5/4,-z+5/4, #3 -y+3/4,x-1/4,-z+3/4.

Table S3. Selected bond angles (°) for compound **1^a**.

Se(1)#1-In(1)-Se(1)	109.30(14)	Se(1)-In(1)-Se(2)	109.90(8)
Se(1)-In(1)-Se(2)#1	108.21(8)	Se(1)#1-In(1)-Se(2)	108.21(8)
Se(1)#1-In(1)-Se(2)#1	109.90(8)	Se(2)#1-In(1)-Se(2)	111.31(12)
Se(2)-In(2)-Se(2)#2	113.16(11)	Se(3)-In(2)-Se(2)	107.03(9)
Se(3)-In(2)-Se(2)#2	109.22(9)	Se(3)-In(2)-Se(4)	106.95(9)
Se(4)-In(2)-Se(2)	110.27(9)	Se(4)-In(2)-Se(2)#2	109.98(9)
Se(1)#1-In(3)-Se(3)#2	117.15(10)	Se(1)#1-In(3)-Se(4)	112.55(11)
Se(1)#1-In(3)-Se(5)	108.14(10)	Se(4)-In(3)-Se(3)#2	111.40(10)
Se(5)-In(3)-Se(3)#2	97.02(9)	Se(5)-In(3)-Se(4)	109.19(10)
Se(5)-In(4)-Se(6)	110.70(10)	Se(5)-In(4)-Se(7)	97.68(9)
Se(5)-In(4)-Se(8)	109.69 (10)	Se(6)-In(4)-Se(7)	111.41(10)
Se(8)-In(4)-Se(6)	113.22 (10)	Se(8)-In(4)-Se(7)	113.10(10)
Se(6)-In(5)-Se(10)	116.35(11)	Se(9)-In(5)-Se(6)	103.36(11)
Se(9)-In(5)-Se(10)	105.02(9)	Se(13)-In(5)-Se(6)	110.44(11)
Se(13)-In(5)-Se(9)	110.60(9)	Se(13)-In(5)-Se(10)	110.62(11)
Se(11)-In(6)-Se(8)	113.74(11)	Se(11)-In(6)-Se(12)	104.54(11)
Se(12)-In(6)-Se(8)	103.90(11)	Se(13)-In(6)-Se(8)	112.69(11)
Se(13)-In(6)-Se(11)	114.16(12)	Se(13)-In(6)-Se(12)	106.62(11)
Se(7)-In(7)-Se(10)	112.42(11)	Se(7)-In(7)-Se(12)#3	99.17(11)
Se(11)-In(7)-Se(7)	116.05(11)	Se(11)-In(7)-Se(10)	108.61(11)
Se(12)#3-In(7)-Se(10)	111.01(11)	Se(11)-In(7)-Se(12)#3	109.24(11)

^a Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1/2,z+0, #2 y+3/4,-x+5/4,-z+5/4, #3 -y+3/4,x-1/4,-z+3/4.

2. Supplementary structural figures of compound 1

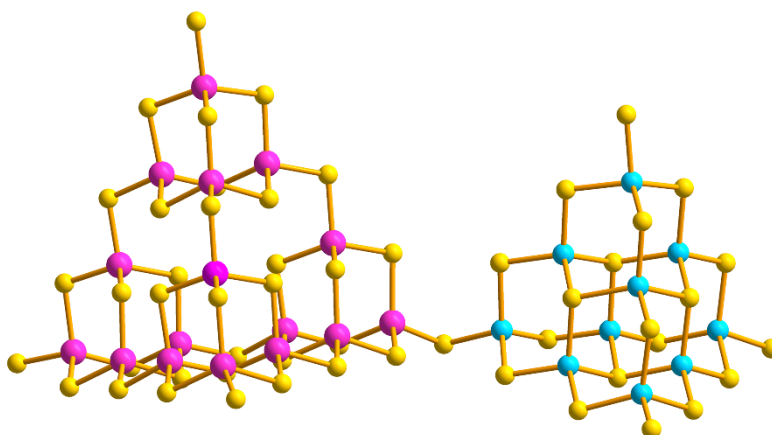


Fig. S1 A view of the anionic clusters of compound **1**. A yellow ball stands for Se, purple for Ge–In mixed sites and light blue for In.

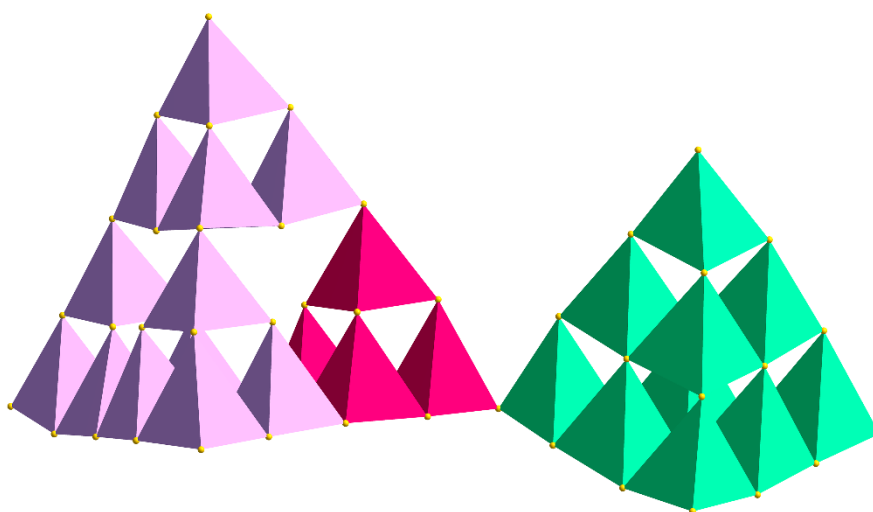


Fig. S2 Coordination motif of the T2 supertetrahedral cluster in compound **1**: one T2 cluster (crimson) connect with three T2 (violet) and one T3 supertetrahedral cluster (green).

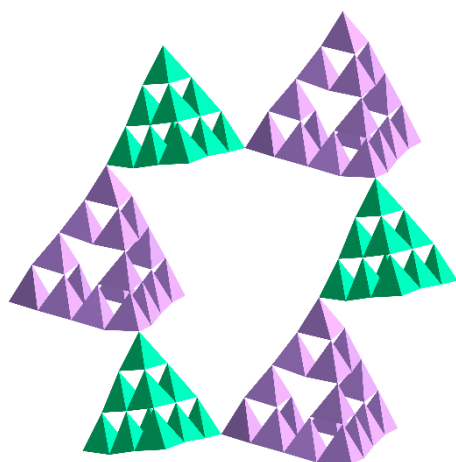


Fig. S3 Three T_{2,2} (violet) super-supertetrahedral and three T₃ (green) supertetrahedral clusters assemble into a six-membered ring with 21 T atoms by sharing selenium atoms on the corner.

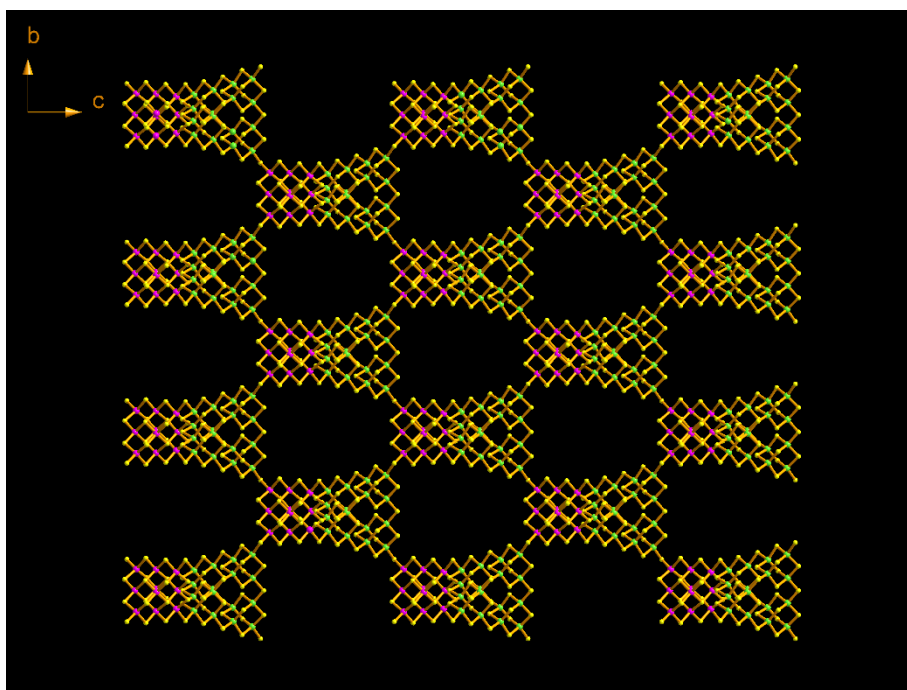


Fig. S4 A view of the 3D framework of compound **1** projected down along *a*-axis. Only one set of superlattice is shown for clarity. A yellow ball stands for Se, green for Ge–In mixed sites and purple for In.

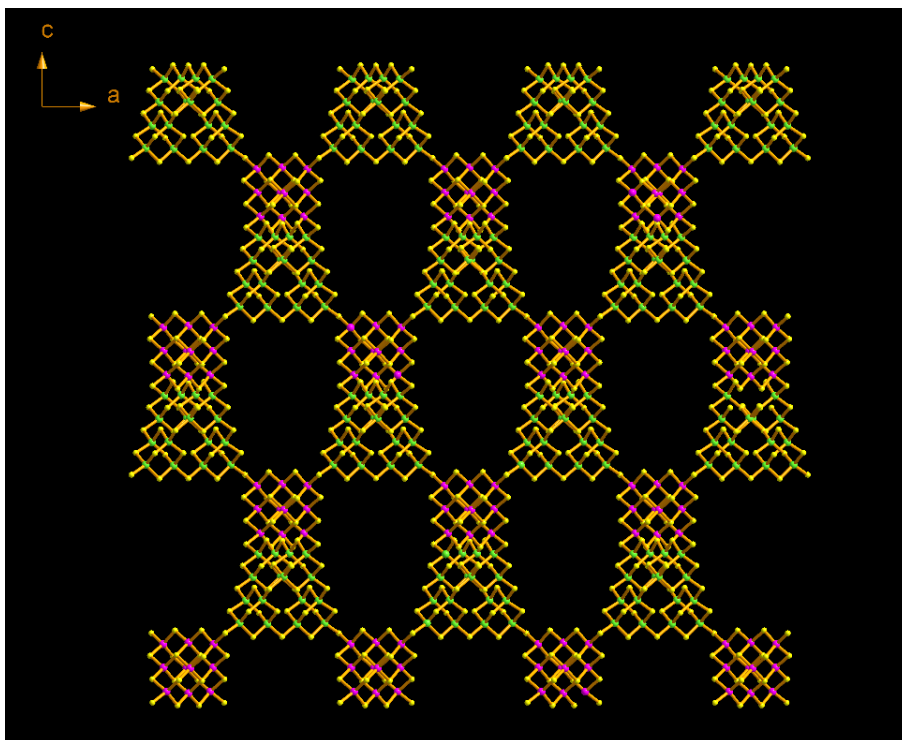


Fig. S5 A view of the 3D framework of compound **1** projected down along b -axis. Only one set of superlattice is shown for clarity. A yellow ball stands for Se, green for Ge–In mixed sites and purple for In.

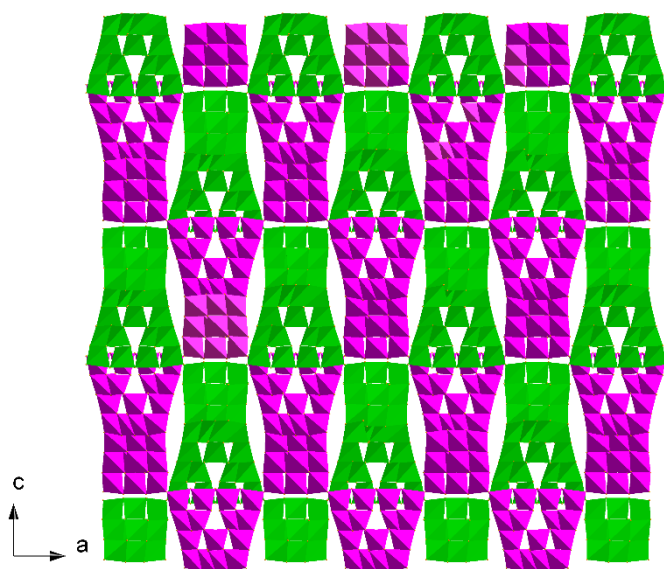


Fig. S6 A fragment structure of the compound **1** containing two interpenetrating diamond lattices (shown in green and purple) viewed along b -axis.

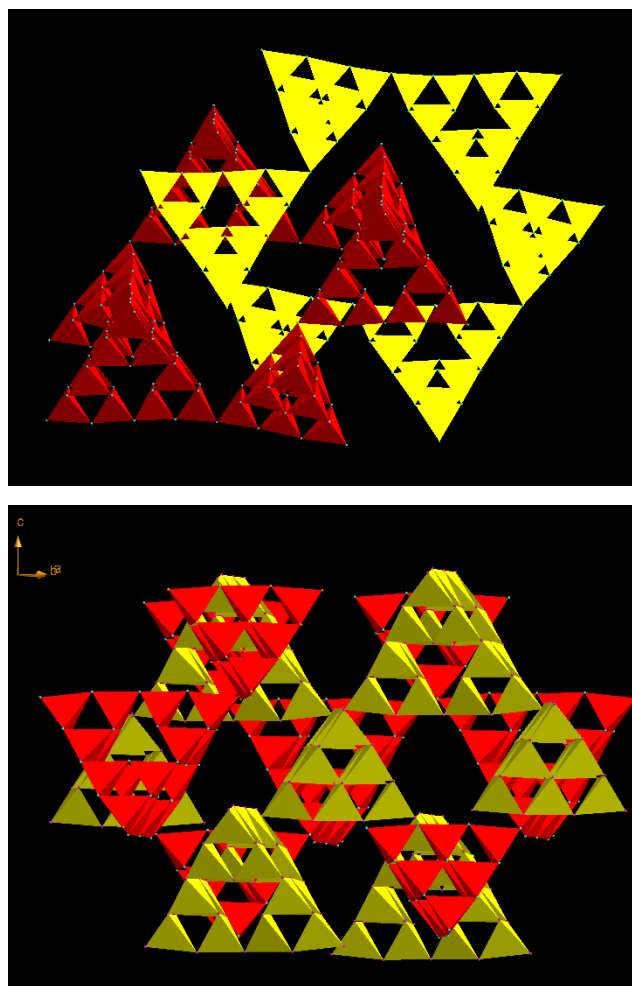


Fig. S7 A view of the interpenetrating mode between the two six-membered ring in **1** (top) and the large channels in this two interpenetrating diamond networks (bottom) shown in red and yellow.

3. Experimental section

All chemicals were reagent grade and used as received without further purification. Distilled water was used throughout.

3.1 Synthesis of compound 1

Compound 1 was synthesized by the solvothermal reaction as follows: 97.31 mg GeO₂ (0.93 mmol), 243.41 mg In (2.12 mmol), 352.162 mg Se (4.46 mmol) were added into 4.0 mL 0.8M Piperazine (PPZ) aqueous solution. The mixture was stirred for 3 h and transferred to a 23 ml Teflon-lined stainless steel autoclave. The vessel was then sealed and heated at 180°C for 10 days without being disturbed. After cooling to room temperature very slowly, the reaction mixture was filtered, washed with ethanol and water, and dried in air at room temperature. The orange-yellow crystals were obtained (yield 10 %, based on In).

3.2 Details of the structure refinement

Semi-quantitative energy dispersive X-ray (EDS) analysis confirmed the presence of all constituent heavy elements in compound 1 and the ICP-MS quantitative analysis gave a Ge/In/Se mole ratio of 1.000/5.701/12.887. Extra-framework species in structure could not be located in the final structural refinement due to their disorder. The final extra-framework species in molecular formula were given from CHN analysis. Calcd: C, 6.30; H, 2.07; N, 3.67. Found: C, 6.20; H, 2.22; N, 3.79.

4. Physical measurements

Semi-quantitative energy dispersive X-ray analysis (EDS) for heavier elements was performed on Bruker Quantax 200 attached to Hitachi S-4800 field emission scanning electron microscopy. Powder X-ray diffraction (XRD) measurement was performed by a Bruker D8 Focus diffractometer with Cu-K α radiation ($\lambda=1.5406$ Å) and a Lynx Eye detector at 298 K. Thermal analysis was conducted on a Pyris Diamond thermal analyzer under a flowing nitrogen atmosphere with a heating rate of 10°C/min in the range of 25-800°C. Optical diffuse reflectance spectrum was measured with a Hitachi U-4100 UV/Vis spectrophotometer by using BaSO₄ powder as the 100% reflectance reference. The absorption data was calculated from the

reflectance using the Kubelka-Munk function [4]. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed on Thermo Scientific iCAP 6000 ICP spectrometer. CHN Analysis was obtained on Vario EL.

4.1 The energy dispersive X-ray spectra (EDS)

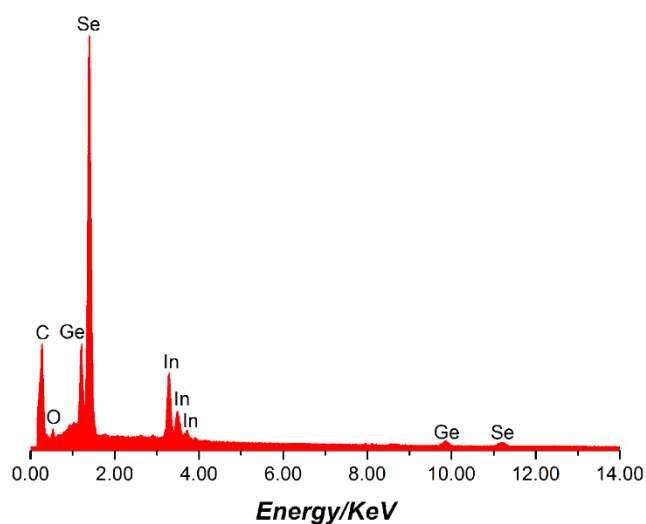


Fig. S8 The energy dispersive X-ray spectra of **1**.

4.2 Powder X-ray diffraction (XRD) pattern

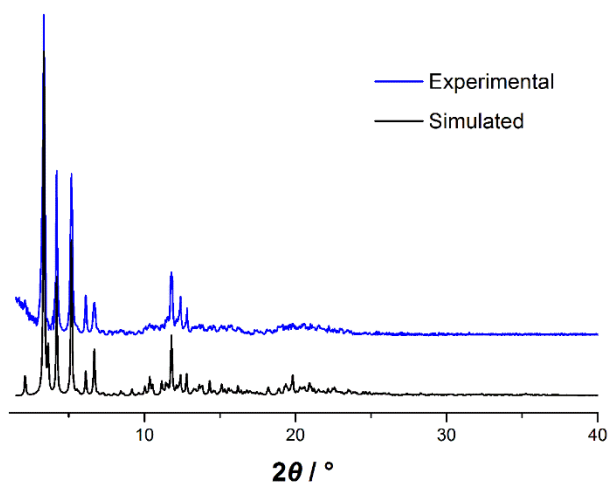


Fig. S9 The PXRD pattern of **1** (top) is comparable with its simulated from the single crystal X-ray data (bottom).

4.3 TGA

The thermal stability of compound **1** was determined by TGA under a nitrogen

atmosphere. The initial weight loss of 4.69% between roomtemperature and 160°C could be attributed to the loss of water molecules adsorbed on the surface or trapped in the pore. Then the following successive weight loss of 11.52% to 447°C corresponds to the decomposition of the the template amine, which result in the sequential collapse of framework.

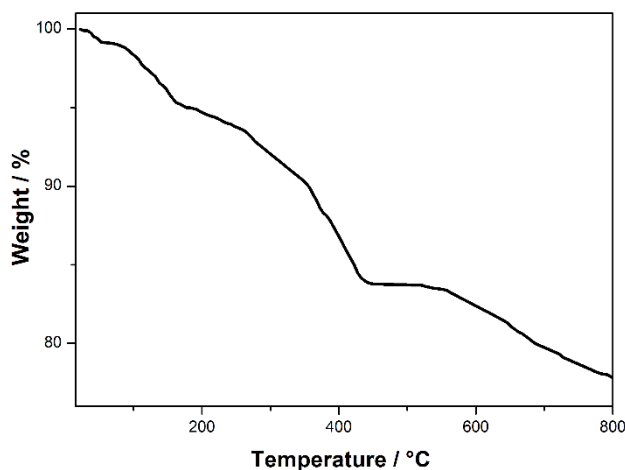


Fig. S10 TGA curve of **1** under N₂ atmosphere

4.4 Solid-state UV/Vis spectra

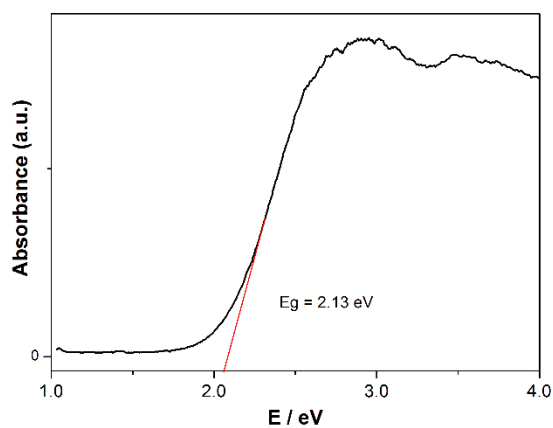


Fig. S11 Solid-state optical absorption spectra of **1**.

Reference

- [1] G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [2] G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- [3] (a) C. Wang, X. Bu, N. Zheng and P. Feng, *Chem. Commun.*, 2002, 1344; (b) T. Wu, X. Wang, X. Bu, X. Zhao, L. Wang and P. Feng, *Angew. Chem., Int. Ed.*, 2009, **48**, 7204.
- [4] W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966.