# $[AEPH_2][GeSb_2S_6]\cdot CH_3OH$: a thiogermanate-thioantimonate featuring an infinite ribbon-like structure with an unusual $\{GeSb_3S_{11}\}$ unit and exhibiting the ability of photocatalytic degradation of organic dye

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## Supporting Information

## 1. Synthesis

$[AEPH_2][GeSb_2S_6]\cdot CH_3OH$ (**1**) was prepared from a mixture of $GeO_2$ (0.052 g, 0.5 mmol), $Sb_2S_3$ (0.165 g, 0.49 mmol), S (0.093 g, 2.90 mmol), 1 mL N-(2-aminoethyl)piperazine and 3 mL $CH_3OH$, which was sealed in a stainless steel reactor with a 20 mL Teflon liner, heated at 160 °C for 7 days and then spontaneously cooled to room temperature. After the product was filtrated, the yellow clubbed crystals of **1** and a small number of indefinite yellow powder were obtained. The crystalline products of **1** were selected by hand, washed by ethanol, and air-dried (Yield: 0.201 g, 61% based on Sb). Anal. calc. for $C_7H_{21}GeN_3OS_6Sb_2$ **1**: C, 12.52%; H, 3.15%; N, 6.26%. Found: C, 12.45%; H, 3.21%; N, 6.64%.

## 2. Crystal Structure

The intensity data of **1** was collected on a Xcalibur E Oxford diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELX97 program package.[1] Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms attached to the C, N and O atoms in compound **1** are located at geometrically calculated positions. The methanol molecule in compound **1** showed positional disorder and was split into two non-equivalent positions with refined SOFs of 0.652(14) and 0.348(14), respectively. The empirical formula was confirmed by the TGA and EA results. Selected bond lengths and angles of compound **1** are listed in Table S1. Selected hydrogen-bonding data of compound **1** are listed in Table S2.

**Table S1.** Selected bond lengths (Å) and angles (°) for [AEPH$_2$][GeSb$_2$S$_6$]·CH$_3$OH (**1**).

| | **1** | | **1** |
|---|---|---|---|
| Sb(1)-S(5) | 2.3690(14) | Sb(2)-S(6)#2 | 2.4409(14) |
| Sb(1)-S(1)#1 | 2.5207(14) | Sb(2)-S(6) | 2.5002(13) |
| Sb(1)-S(3) | 2.5279(14) | Sb(2)-S(2) | 2.6034(14) |
| Ge(1)-S(4) | 2.1503(16) | Sb(2)-S(5)#3 | 2.9308(16) |
| Ge(1)-S(2) | 2.2211(15) | Sb(2)-S(5) | 3.1810(15) |
| Ge(1)-S(1) | 2.2234(14) | | |
| Ge(1)-S(3) | 2.2573(13) | | |
| | | | |
| S(5)-Sb(1)-S(1)#1 | 93.46(5) | S(6)#2-Sb(2)-S(6) | 90.66(4) |
| S(5)-Sb(1)-S(3) | 95.68(5) | S(6)#2-Sb(2)-S(2) | 87.78(5) |
| S(1)#1-Sb(1)-S(3) | 89.31(5) | S(6)-Sb(2)-S(2) | 84.74(4) |
| S(4)-Ge(1)-S(2) | 111.65(5) | S(6)#2-Sb(2)-S(5)#3 | 85.48(5) |
| S(4)-Ge(1)-S(1) | 115.62(6) | S(6)-Sb(2)-S(5)#3 | 89.61(4) |
| S(2)-Ge(1)-S(1) | 110.12(6) | S(2)-Sb(2)-S(5)#3 | 171.16(4) |
| S(4)-Ge(1)-S(3) | 108.88(6) | S(6)#2-Sb(2)-S(5) | 85.06(4) |
| S(2)-Ge(1)-S(3) | 106.45(6) | S(6)-Sb(2)-S(5) | 170.75(4) |
| S(1)-Ge(1)-S(3) | 103.40(5) | S(2)-Sb(2)-S(5) | 86.89(4) |
| | | S(5)#3-Sb(2)-S(5) | 98.21(4) |

Symmetric codes: #1 *x*+1, *y*, *z*; #2 *x*+1/2, *y*, -*z*+1/2; #3 *x*-1/2, *y*, -*z*+1/2.

**Table S2.** Selected hydrogen bonds data for [AEPH$_2$][GeSb$_2$S$_6$]·CH$_3$OH (**1**).

| D–H···A | D-H (Å) | H···A (Å) | D···A (Å) | <(DHA) (°) |
|---|---|---|---|---|
| N(1)-H(1C)...S(3) | 0.90 | 2.69 | 3.521(5) | 153.7 |
| N(1)-H(1C)...S(5) | 0.90 | 2.92 | 3.513(5) | 124.6 |
| N(1)-H(1D)...O(1) | 0.90 | 1.86 | 2.729(12) | 160.4 |
| N(1)-H(1D)...O(1B) | 0.90 | 1.96 | 2.777(14) | 150.1 |
| N(3)-H(3C)...S(4)$^{i}$ | 0.89 | 2.32 | 3.204(5) | 171.3 |
| N(3)-H(3D)...S(4)$^{ii}$ | 0.89 | 2.52 | 3.345(5) | 153.6 |
| N(3)-H(3E)...S(3)$^{iii}$ | 0.89 | 2.71 | 3.339(5) | 128.4 |
| N(3)-H(3E)...S(4)$^{iii}$ | 0.89 | 2.78 | 3.547(5) | 144.7 |

Symmetry codes: i -*x*+1, -*y*, -*z*; ii -*x*+1/2, *y*-1/2, *z*; iii -*x*+3/2, *y*-1/2, *z*.

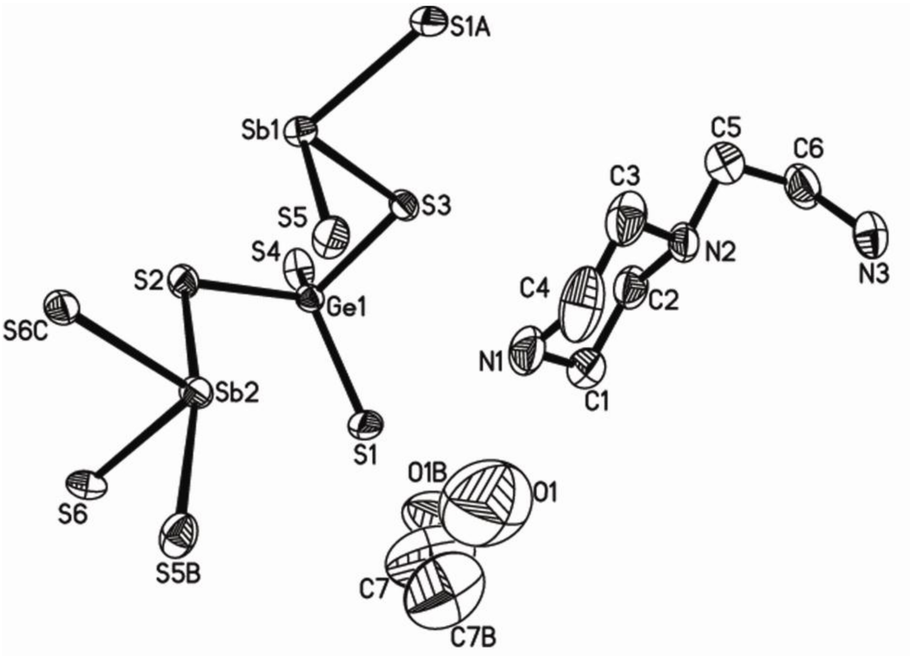
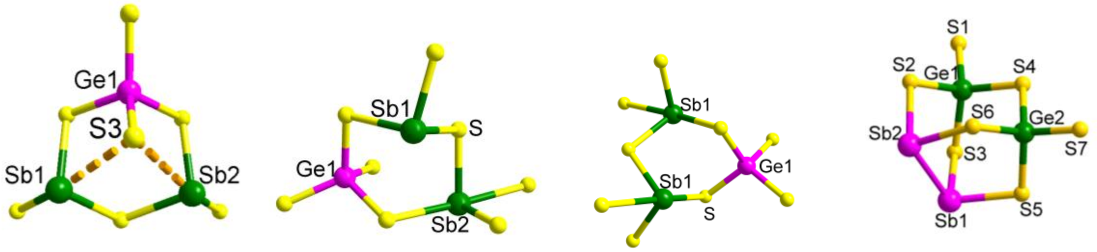
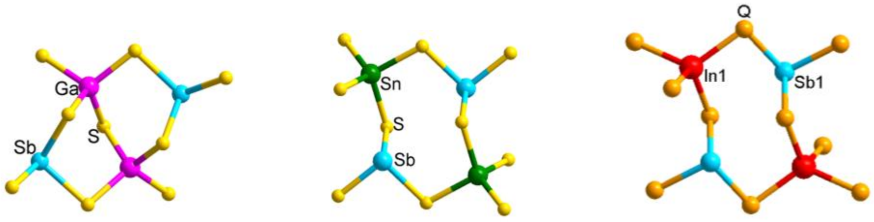


**Fig. S1** *ORTEP* plot showing the crystallographically asymmetric unit of **1** and the coordination geometries of metal ions; thermal ellipsoids are given at the 50% probability level. Symmetry codes for generated atoms: A) 1+*x*, *y*, *z*; B) *x*-1/2, *y*, 1/2-*z*; C) *x*+1/2, *y*, 1/2-*z*.



(a) {GeSb$_2$S$_7$} (b) {GeSb$_2$S$_8$} (c) {GeSb$_2$S$_9$} (d) {Ge$_2$Sb$_2$S$_7$}

**Fig. S2** (a) {GeSb$_2$S$_7$} unit in 2D-[Co(dien)$_2$]$_2$GeSb$_4$S$_{10}$ (dien = diethylenetriamine);[2] (b) {GeSb$_2$S$_8$} unit in 1D-[(Me)$_2$NH$_2$][DabcoH]$_2$[Ge$_2$Sb$_3$S$_{10}$] (Dabco = triethylenediamine), 2D-[M(en)$_3$][GeSb$_2$S$_6$] (M = Mn, Co, Ni, Ge; en = ethylenediamine);[2-4] (c) $\{GeSb_2S_9\}$ unit in 3D-$[(Me)_2NH_2]_2GeSb_2S_6$;[5] (d) $\{Ge_2Sb_2S_7\}$ unit in 0D-$[Me_2NH_2]_6[(Ge_2Sb_2S_7)(Ge_4S_{10})]$.[3]



(a) $\{Ga_2Sb_2S_9\}$ (b) $\{Sn_2Sb_2S_{10}\}$ (c) $\{In_2Sb_2Q_{10}\}$ (Q = S, Se)

**Fig. S3** (a) The tetranuclear heterometallic unit of $\{Ga_2Sb_2S_9\}$ in $[Ni(en)_3][Ga_2Sb_2S_7]$, $[(Me)_2NH_2]_2[Ga_2Sb_2S_7]$[6] and $[(Me)_2NH_2]_2[Ga_2Sb_2S_7]\cdot H_2O$;[7] (b) the tetranuclear heterometallic unit of $\{Sn_2Sb_2S_{10}\}$ in $[La(en)_4SbSnS_5]_2\cdot 0.5H_2O$;[8] (c) the tetranuclear heterometallic unit of $\{In_2Sb_2Q_{10}\}$ (Q = S, Se) in $[(Me)_2NH_2]_2[In_2Sb_2S_{7-x}Se_x]$ ($x$ = 0, 2.20, 4.20, and 7).[9]

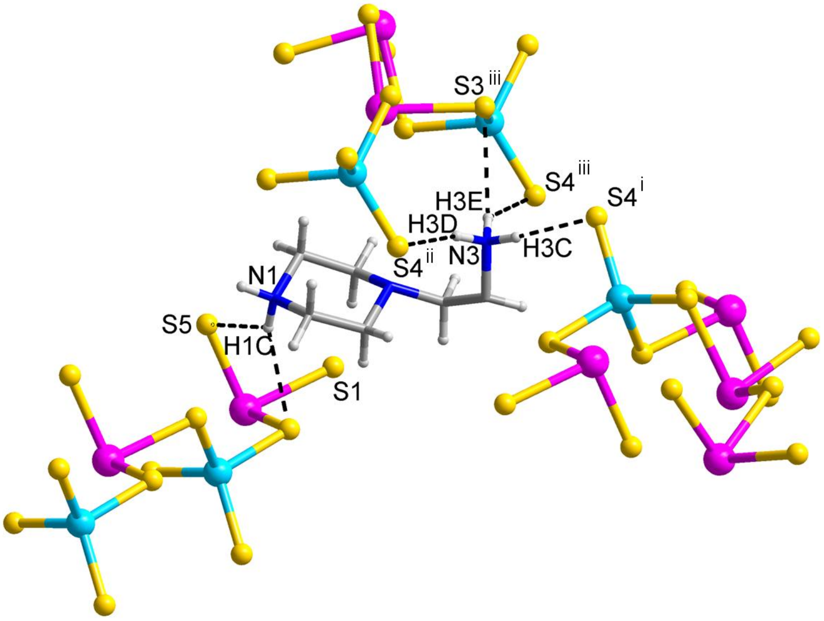


**Fig. S4** The doubly protonated N-(2-aminoethyl)piperazine cations form N–H···S hydrogen bonds with sulfur atoms from adjacent three double ribbons of $[GeSb_2S_6]_n^{2n-}$. The N–H···S hydrogen bond distances and angles fall in the range of 3.204(5) to 3.547(5) Å and 124.6 to 171.3°, respectively. Symmetry codes: i $-x+1, -y, -z$; ii $-x+1/2, y-1/2, z$; iii $-x+3/2, y-1/2, z$.

## 3. Physical measurements

All chemicals employed in this study were analytical reagents and commercially available without further purification. Elemental analyses of C, H, N were performed on a German Elementary Vario EL III instrument. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex II diffractometer using Cu*Kα* radiation. Optical diffuse reflectance spectrum was measured at room temperature with a Perkin-Elmer Lambda 900

UV/Vis spectrophotometer in the range of 200-1100 nm. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra by using the Kubelka-Munk function: $a/S = (1-R)^2/2R$,[10] 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 analysis was carried out with a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min under a nitrogen atmosphere.

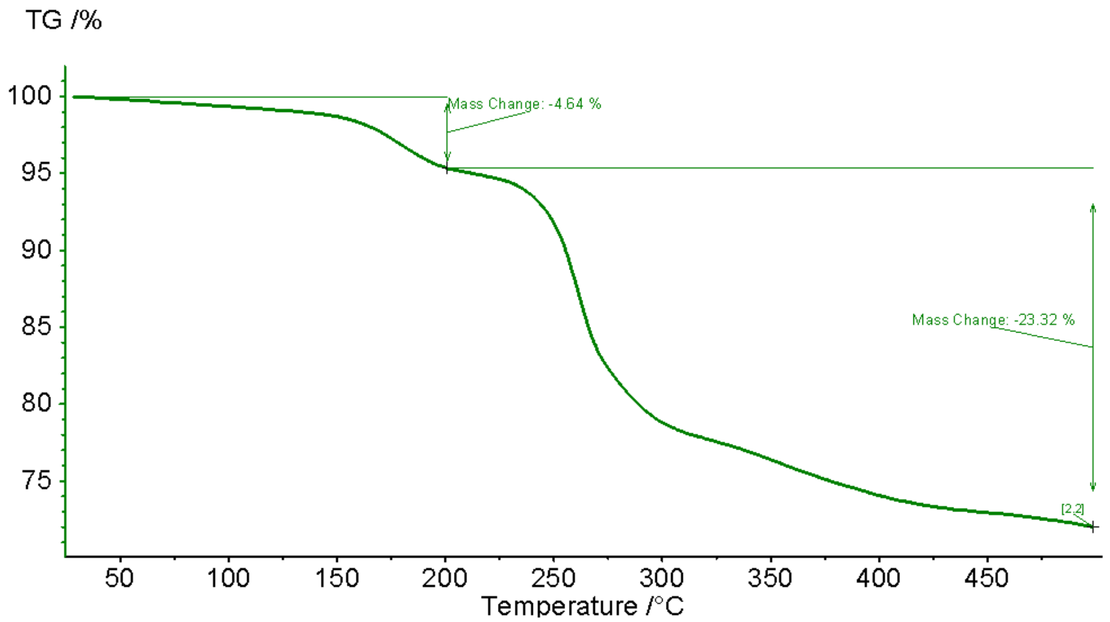


**Fig. S5** Thermogravimetric curve for **1**.

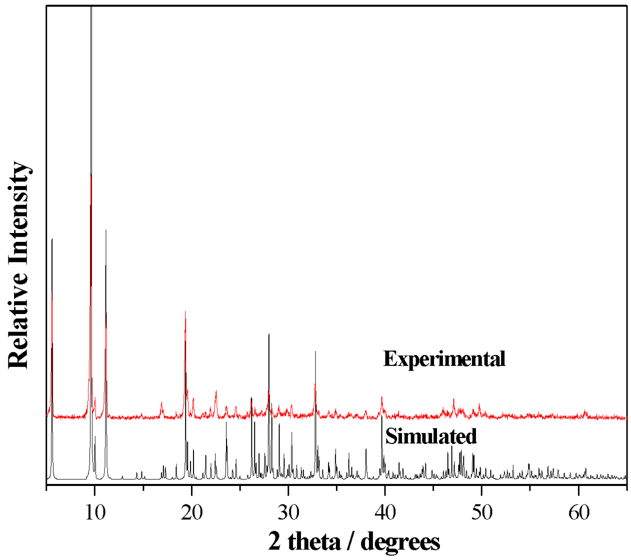


**Fig. S6** The PXRD pattern of **1** (red) is in good agreement with that simulated from single crystal X-ray data of **1** (black).

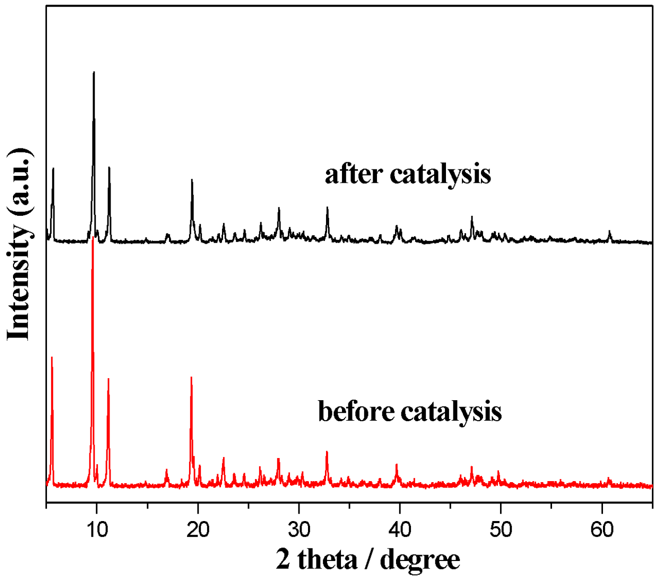


**Fig. S7** The PXRD pattern of **1** after catalysis (black) is in good agreement that of **1** before catalysis (red).

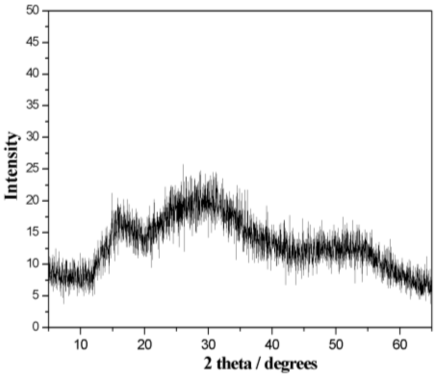


**Fig. S8** The PXRD pattern of the TG residue of **1**

## 4. Theoretical band structure

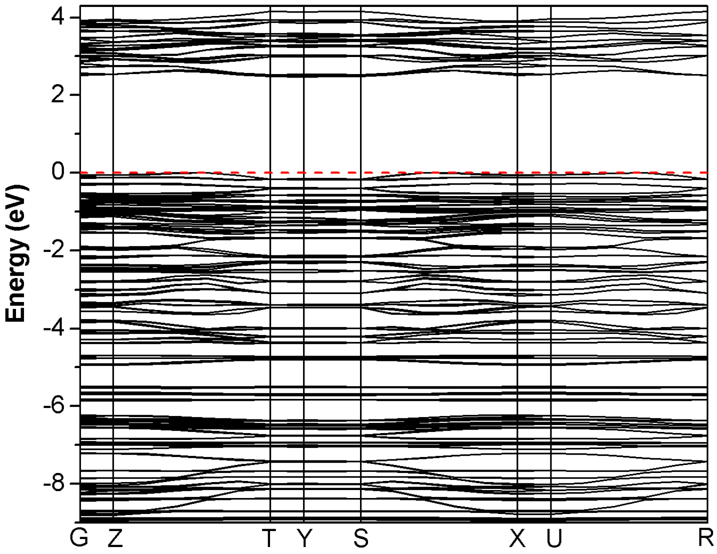


**Fig. S9** The band structure of **1**. Fermi level is set at 0 eV (red dot line).

**Table S3.** The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of **1**.

| k-point | L-CB | H-VB |
|---|---|---|
| G (0.000, 0.000, 0.000) | 2.51161 | -0.04854 |
| Z (0.000, 0.000, 0.500) | 2.53161 | -0.05957 |
| T (-0.500, 0.000, 0.500) | 2.4898 | -0.1639 |
| Y (-0.500, 0.000, 0.000) | 2.4747 | -0.15497 |
| S (-0.500, 0.500, 0.000) | 2.49107 | -0.1572 |
| X (0.000, 0.500, 0.000) | 2.51578 | -0.04959 |
| U (0.000, 0.500, 0.500) | 2.53639 | -0.05979 |
| R (-0.500, 0.500, 0.500) | 2.50493 | -0.16587 |

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