Supplementary information

Chemical routes to GeS$_2$ and GeSe$_2$ nanowires

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Synthesis of [C$_6$H$_{14}$NH$_2$]$_4$Ge$_2$Se$_6$:

In a typical synthesis, 158.7 mg (~2mM) of metallic Se was added to 9.5 ml of di-propylamine and stirred for ~1 h. 72.8 mg (~1mM) of metallic Ge was added to this solution and the entire reaction mixture was transferred to a 23ml acid-digestion bomb and sealed in an autoclave, which was then heated to 180°C for 5d. The autoclave was then cooled to room temperature and the bright yellow crystals of [C$_6$H$_{14}$NH$_2$][Ge$_2$Se$_6$] were filtered and dried under vacuum. It should be noted that the product was extremely moisture and air-sensitive and readily decomposed to Se on exposure to atmosphere for several hours. The product was stored in a dessicator under Ar atmosphere.

Characterization of [C$_6$H$_{14}$NH$_2$][Ge$_2$Se$_6$]:

Single Crystal X-ray Structure Determination:

A suitable single crystal of the compound was selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed with a Siemens smart – CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda$=0.71073 Å) operating at 50 kV and 40 mA. The structure was solved by direct methods using SHELXS-86 [G. M. Sheldrick, SHELXS-86 Program for Crystal Structure Determination, University of Gottingen, Gottingen, Germany, (1986)], which readily established the heavy atom positions (Ge and Se) and facilitated the identification of the light atoms (C, N) from difference Fourier maps. All the hydrogen positions were initially observed in the difference Fourier maps, but for the final refinement the hydrogen atoms of the amine were placed geometrically and held in the riding mode. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against |F$^2$| was carried out using SHELXTL-PLUS package of programs [G. M. Sheldrick, SHELXS-93 Program for Crystal Structure Solution and Refinement, University of Gottingen, Gottingen, Germany (1993)]. The final crystallographic parameters can be found in the CIF file.
Powder X-ray Diffraction (PXRD): The purity of the bulk product (the yellow crystalline solid) was determined by experimental PXRD which is in good agreement with the simulated powder pattern generated by using the coordinates of single crystal data.

IR, CHN and Thermogravimetric Analysis: IR spectrum shows broad bands in the region 3300-3500cm⁻¹ (–N-H stretching of the secondary amine), 2700-2900 and 1400-1650cm⁻¹ (the stretching and bending modes of -CH₂- group), and weak bands in the region 950-1150cm⁻¹ (–C-N stretching). C,H,N analysis: C (18.81%) H (4.26%) and N (2.82%). The relative amount of the amine calculated from the C,H,N data was lower than the composition [C₆H₁₄NH₂]₄[Ge₂Se₆] obtained from single crystal data. This may be due to the decomposition of the compound on longer exposure to air/atmosphere. The TGA analysis shows two steps at ~150°C and ~450°C accounting for a total loss of ~46.8%, presumably due to the loss of amine and the Se.

Structure description: [C₆H₁₄NH₂]₄[Ge₂Se₆] crystallized in a monoclinic P2₁/c space group with a=10.8528(8)Å, b=18.3953(14)Å, c=10.9941(8)Å and β=103.425°. The crystal structure of [(C₃H₇)₂NH₂][Ge₂Se₆] consists of isolated cations (dipropylammonium ions) and [Ge₂Se₆]⁴⁻ anion, which is an edge-shared dimer of GeSe₄ tetrahedra (Fig. S1). There is evidence of weak Se…H-N (Se…H = 2.492(9) – 2.449(9)Å) interaction between the cations and anions, other than van der Waals and ionic attraction in the 3D crystalline assembly.

Fig. S1: The structure of the molecular precursor [C₆H₁₄NH₂]₄[Ge₂Se₆] showing the [Ge₂Se₆] dimer and the amine.