## Supplementary Materials

## Metal-insulator transition in quasi-one-dimensional HfTe<sub>3</sub> in the few-chain limit

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## Materials

Carbon nanotubes are purchased from CheapTubes (90% SW-DW CNTs), Hafnium powder from Fisher Scientific (99.6%, 325 mesh), Tellurium shot from Sigma-Aldrich (99.999%, 1-2mm), and Iodine from Spectrum Chemicals (99.8%, resublimed).

Transmission Electron Microscopy (TEM) Characterization

After synthesis, filled carbon nanotubes are cast onto lacey carbon TEM grids for characterization. A JEOL 2010 microscope (80 kV) is used for high-resolution imaging (HR-TEM), Titan-X (80 kV) for energy dispersive spectroscopy (EDS), and TEAM 0.5 (aberration corrected, 80 kV) for scanning transmission electron microscopy (STEM) imaging.



**FIG. S1. Encapsulation of single HfTe<sub>3</sub> chains.** Scanning transmission electron microscopy image of (a-c) single HfTe<sub>3</sub> chains encapsulated within a carbon nanotube. (a) and (c) show the same single-chain HfTe<sub>3</sub>, however (c) is shown in low contrast where the CNT walls are visible. Hf and Te atoms appear white in the images. An atomic model below demonstrates the orientation of the chain in both A and B, where Hf and Te atoms are red and green, respectively. Scale bars measure 1 nm.

## Calculation Methods

We perform first-principles calculation based on density functional theory (DFT). We use the generalized gradient approximation, [9] norm-conserving pseudopotentials, [10] and localized pseudo-atomic orbitals for the wavefunction expansion as implemented in the SIESTA code. [11] The spin-orbit interaction is considered using fully relativistic j-dependent pseudopotentials [12] in the 1-dependent fully-separable nonlocal form using additional Kleinman-Bylander-type projectors. [13,14] We use 1×512×1 Monkhorst-Pack k-point mesh for finite chains, and 40×64×24 for bulk. Real-space mesh cut-off of 1000 Ry is used for all of our calculations. The van der Waals interaction is evaluated using the DFT-D2 correction. [15] For finite chains, a vacuum region of 50 Å  $\times$  50 Å perpendicular to the chain is used and dipole corrections are included to reduce the fictitious interactions between chains generated by the periodic boundary condition in our supercell approach. [16]



FIG. S2. Calcuated atomic and electronic structures of HfTe<sub>3</sub> bulk and finite parallel

**chains.** The atomic and electronic structures of HfTe<sub>3</sub> bulk crystal and parallel finite chains with TP geometry isolated in vacuum are presented. (a-c) The bulk crystal, (d-f) 22-chain, (g-i) quadruple-chain, (j-l) triple-chain, (m-o) double-chain, and (p-r) single-chain. In the axial view along the *b*-axis of the unit cell, the red and green spheres represent Hf and Te atoms, respectively. In the band structures, the chemical potential is set to zero and marked with a horizontal dashed line and the Brillouin zone center and the edge are denoted as  $\Gamma$  and *Z*, respectively.

To compare the stability of isosceles vs. equilateral distribution of the Te atoms in HfTe<sub>3</sub>, we also investigate the atomic and electronic structure of the TP single-chain HfTe<sub>3</sub> with Te

atoms distributed in an equilateral triangle, as shown in Fig. S3a-c. Calculation results from the TP single-chain HfTe<sub>3</sub> with equilateral distribution of the Te atoms indicates that the chain is metallic and has 0.193 and 0.672 eV/f.u. higher total energy than the semiconducting isosceles distribution of Te atoms in TP and TAP single-chain HfTe<sub>3</sub>, respectively.



FIG. S3. Calcuated atomic and electronic structures of TP and TAP geometry single-chain HfTe<sub>3</sub> with Te atoms forming equilateral and isoceles triangles. The atomic and electronic structures of single-chain HfTe<sub>3</sub> isolated in vacuum are presented. (a-c) The TP single-chain HfTe<sub>3</sub> with an equilateral triangle distribution of Te atoms, (d-f) the TP and (g-i) TAP singlechain HfTe<sub>3</sub> with an isosceles triangle distribution of Te atoms. In the axial view along the *b*axis of the unit cell, the red and green spheres represent Hf and Te, respectively. In the band structures, the chemical potential is set to zero and marked with a horizontal dashed line and the Brillouin zone center and the edge are denoted as  $\Gamma$  and Z, respectively. In (h), the bands are unfolded with respect to the first Brillouin zone of the unit cell of the single-chain with length of b<sub>0</sub>.



**FIG. S4. Calcuated atomic and electronic structures of TP geometry single-chain HfTe**<sup>3</sup> **encapsulated a CNT.** (a-b) The atomic and (c-d) electronic structures of TP geometry singlechain HfTe<sub>3</sub> encapsulated in an (8,8) CNT are presented. The atomic structure is obtained with a constraint to force the TP symmetry in the atomic structure optimization. In (c-d), the Fermi energy is set to zero and marked with a horizontal dashed line. In (d), the bands represented by red and grey line are projected onto the chain and CNT, respectively, and unfolded with respect to the first Brillouin zone of the unit cells of the single-chain and CNT, where zone boundaries for the chain and CNT are denoted as Z<sub>HfTe3</sub> and Z<sub>CNT</sub>, respectively.