Supplementary Information

Hexagonal Layered Group IV-VI Semiconductors and Derivatives: Fresh Blood of 2D Family

Xiao-Qing Tian,[ac] Jin-Yi Duan,[a] Maryam Kiani,[a] Ya-Dong Wei,[a] Naixing Feng[b], Zhi-Rui Gong,[a] Xiang-Rong Wang,*[c] Yu Du,*[a] and Boris I. Yakobson*[d]

[a]*College of Physics and Optical Engineering, Shenzhen University, Shenzhen 518060, Guangdong, P. R. China.*

[b]*College of Electronic Sciences and Technology, Shenzhen University, Shenzhen 518060, Guangdong, P. R. China.*

[c]*Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.*

[d]*Department of Materials Science and NanoEngineering, Department of Chemistry, and the Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United States.*

1. The lattice constant dependent energetics of hexagonal group IV-VI semiconductors.

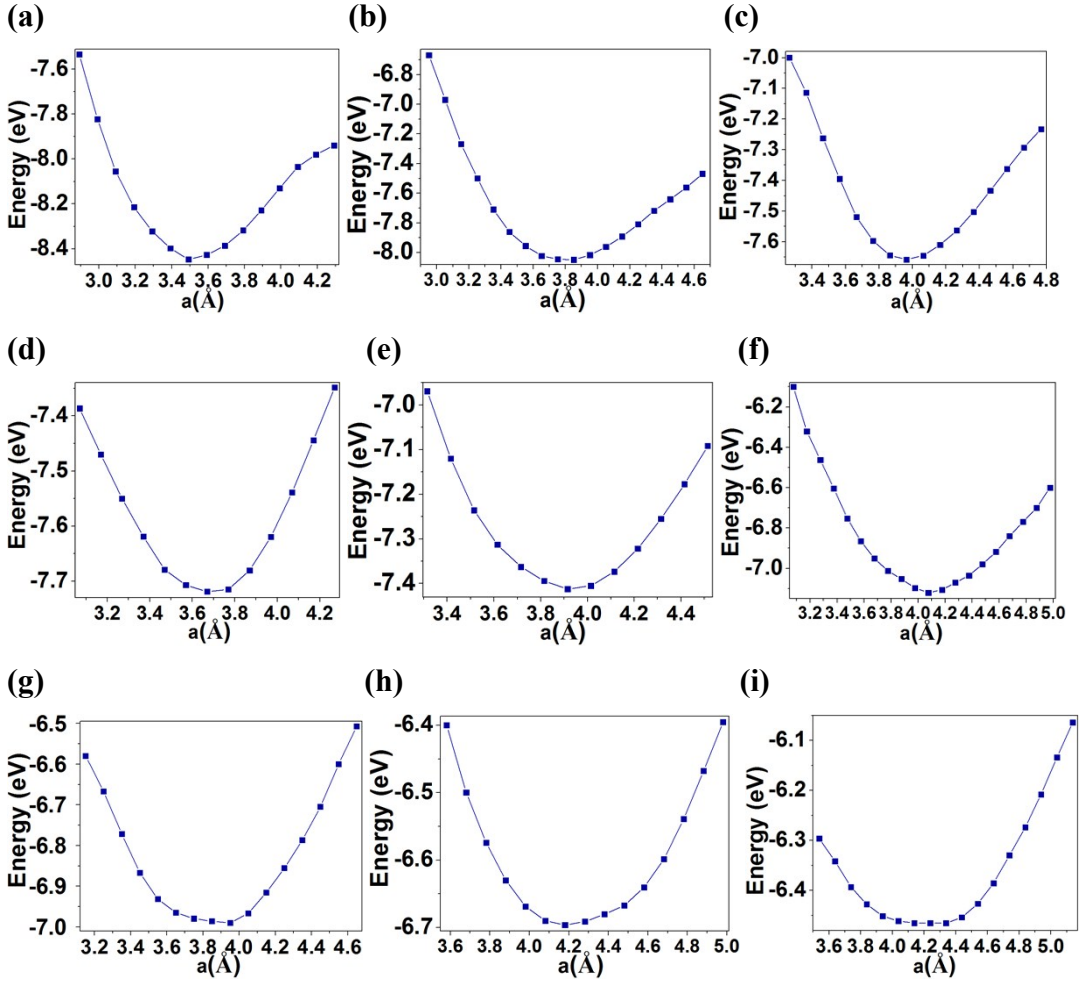

Figure S1.The lattice constant dependent total energies of (a) GeS, (b) SnS, (c) PbS, (d) GeSe, (e) SnSe, (f) PbSe, (g) GeTe, (h) SnTe, and (i) PbTe.

The strain energies in stretched and compressed group IV-VI semiconductors are shown in Figure S1. The deformation energies, shown as a function of the lattice constants in Figure S1, allow judging the influence of in-plane tensile and compressive strain on group IV-VI semiconductors. The variable cell optimization method is also used to search the lattice constant and the results are also in good agreements with the Table S1.

Table S1. Summary of the lattice constants of the group IV-VI semiconductors.

	GeS	SnS	PbS	GeSe	SnSe	PbSe	GeTe	SnTe	PbTe
a(Å)	3.492	3.753	3.965	3.670	3.916	4.076	3.950	4.181	4.338

2. Molecular dynamics study of the stabilities of halogens functionalized SnSe.

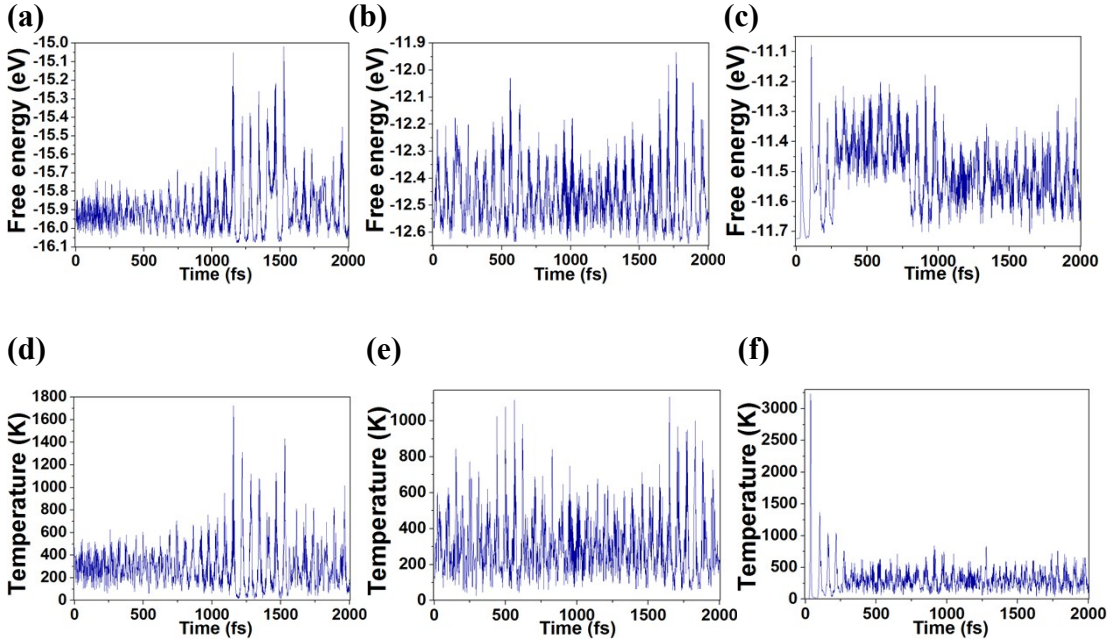

Figure S2. Stabilities of halogens functionalized SnSe studied by quantum molecular dynamics. Fluctuations of free energies of (a) F, (b) Cl, and (c) Br functionalized SnSe; fluctuations of temperatures of (c) F, (d) Cl, and (e) Br functionalized SnSe.

Are the halogens functionalized SnSe stable such as the structures in Figure. 4a and 4b of the manuscript? To answer this question we carried out molecular dynamics simulations with the quantum effects considered at room temperature 300 K with a time step of 1 fs.[1] The structures of SnSe with both top and bottom surfaces functionalized with halogens are investigated. After running 2000 steps, the geometries of all halogens functionalized SnSe are still kept. The total energy variation is smaller than 1.1 eV for all the structures. The temperature variation is in a large range. Even at 3000K, the thermo fluctuation energy is around 0.26 eV. The adsorption energis of halogen adatoms on SnSe are all larger than 3.0 eV which is an order larger than thermo fluctuation energy.

[1] R. Car and M. Parrinello, Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.***1985,** 55, 2471.