Electronic Supplementary Material (ESI) for Nanoscale.

Two-dimensional TiB_4 Monolayer Exhibits Planar Octacoordinate Ti

Xin Qu,[a,b] Jian Lv,*[c] Yanchao Wang,[c,d] Jinghai Yang*[e], Zhongfang Chen[f] and Yanming Ma[d]

[a.] *Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China.*

[b.] *University of Chinese Academy of Sciences, Beijing 100039, P. R. China.*

[c.] *College of Materials Science and Engineering, Jilin University, Changchun 130012, China. E-mail: lvjian@calypso.cn*

[d.] *State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012 China.*

[e.] *Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, PR China. jhyang1@jlnu.edu.cn*

[f.] *Department of Chemistry, Institute for Functional Nanomaterials, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico 00931, United States.*

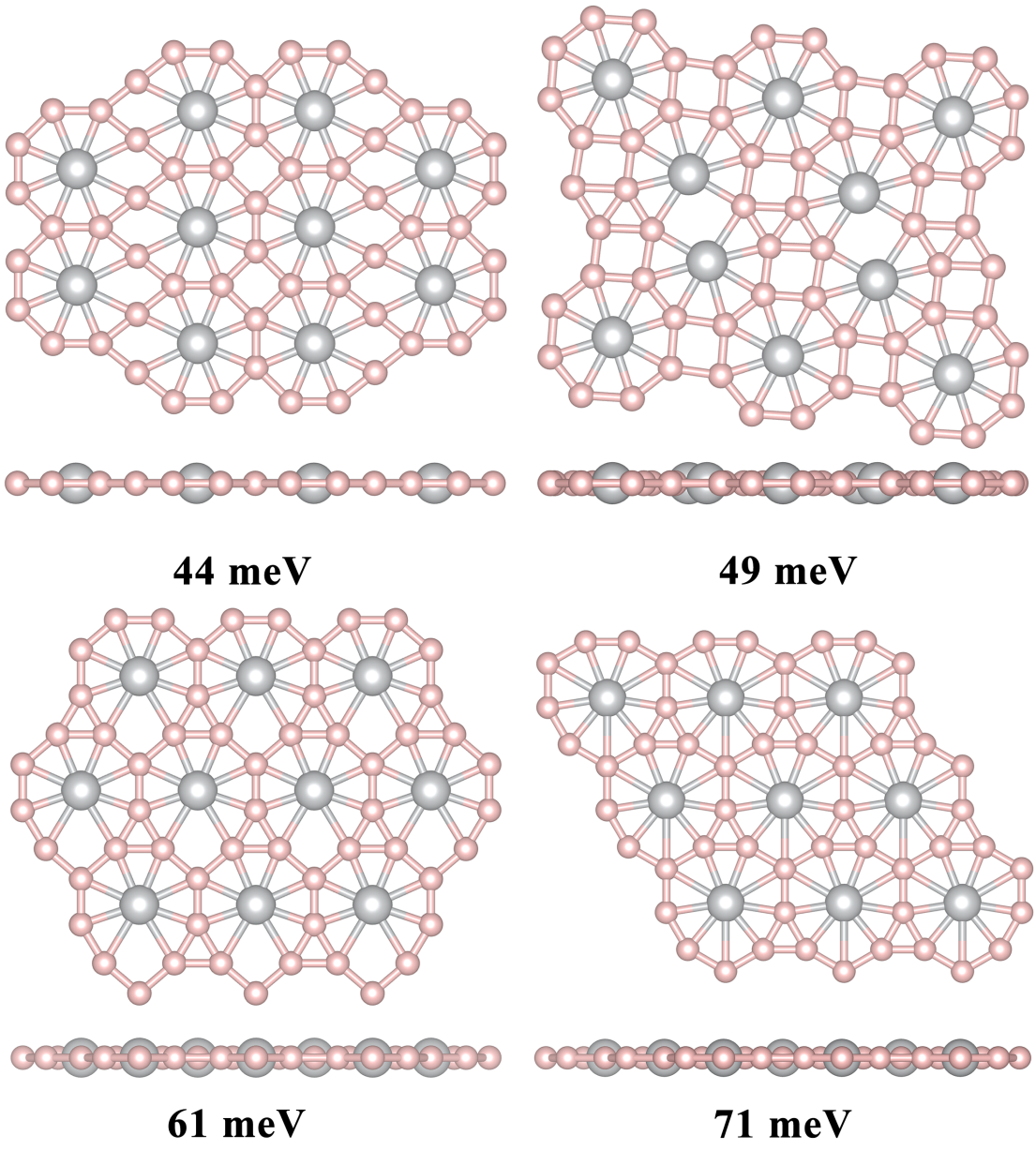

Fig. S1. Low-lying isomers found by the CALYPSO structure search. Ti and B atoms are denoted by grey and pink spheres. Energies relative to the global minimum are labeled.

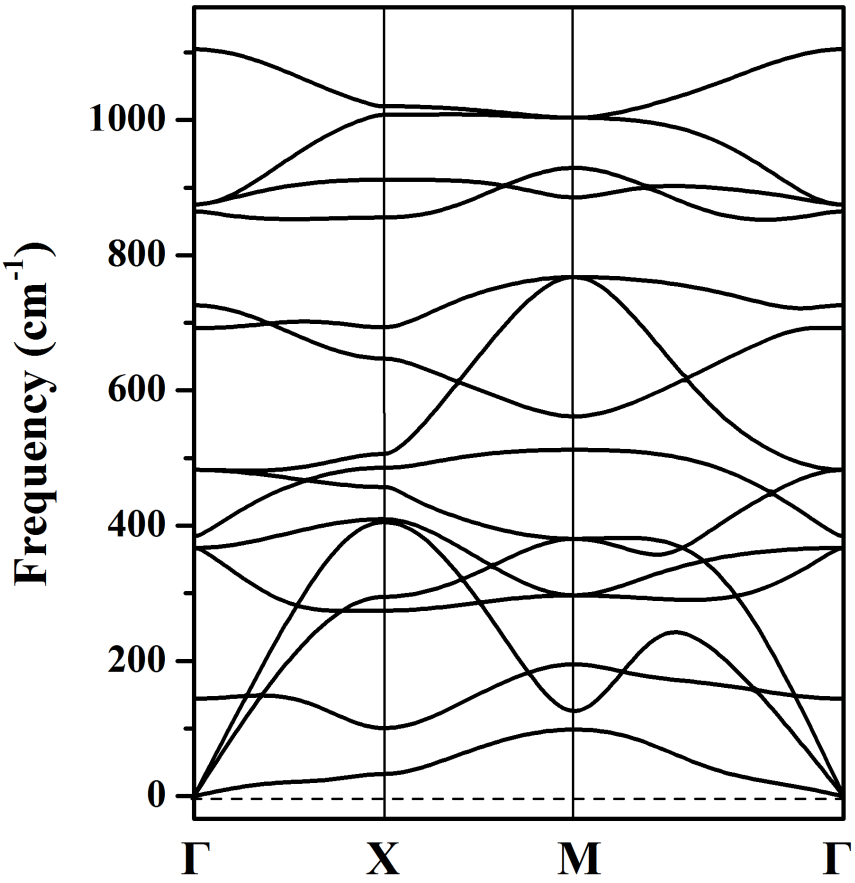

Fig. S2. Phonon dispersion of the lowest-energy structure of the TiB_4 monolayer. Γ (0, 0, 0), X (0.0 0.5 0.0), and M (0.5 0.5 0.0) refer to special q-points in the first Brillouin zone in reciprocal space.

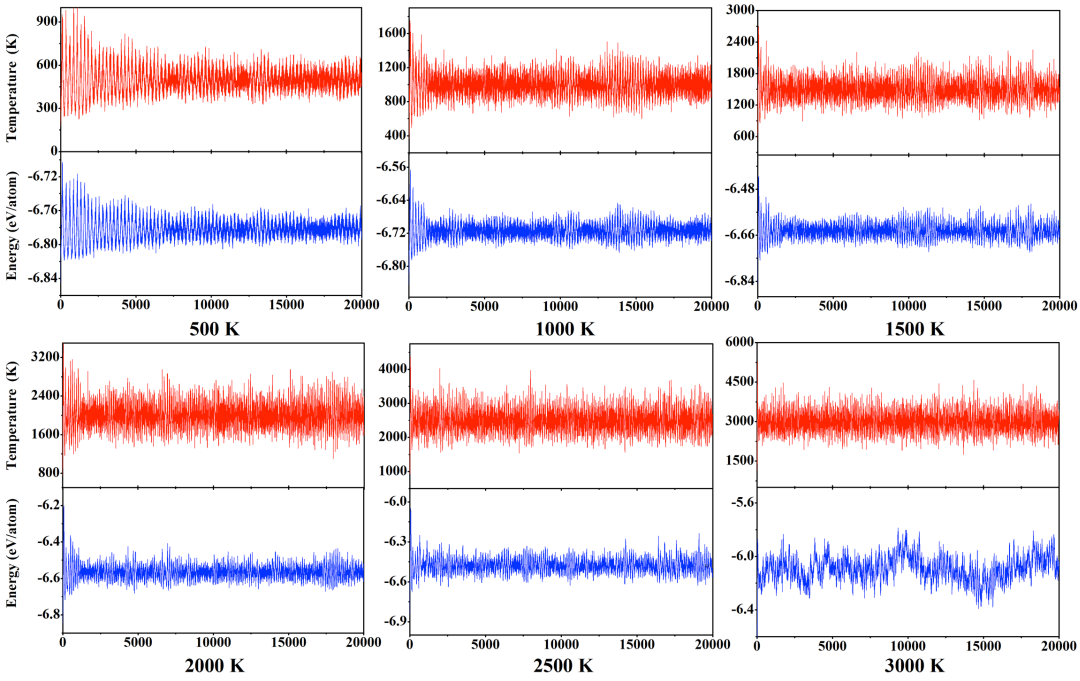

Fig. S3. Temperature/energy fluctuations depending on simulated time in molecular dynamics simulations at temperatures from 500 K to 3000 K for the TiB_4 monolayer.

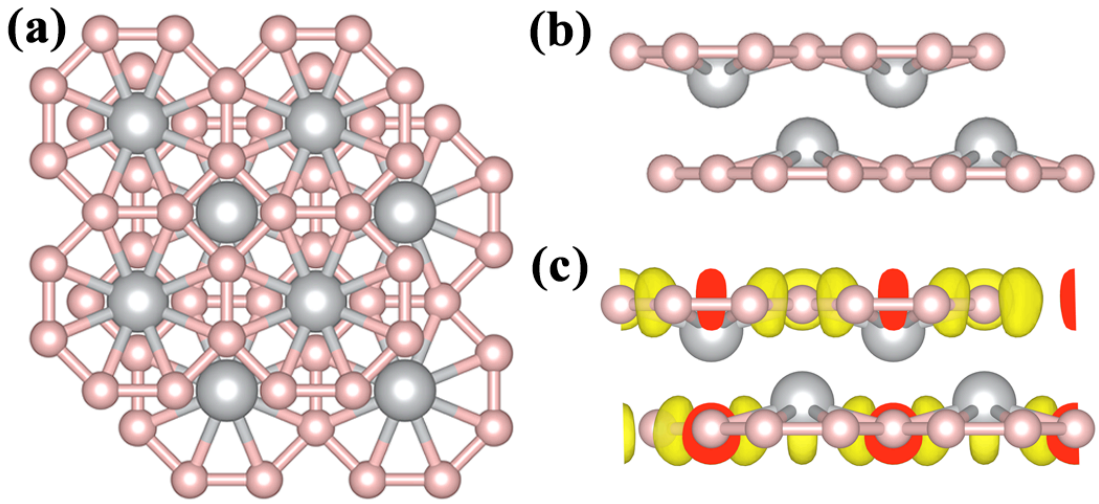

Fig. S4. (a) Top and (b) side views of the ball and stick model of the most stable double-layer stacking of TiB_4 monolayers. (c) Isosurface of ELF plotted with a value of 0.75.

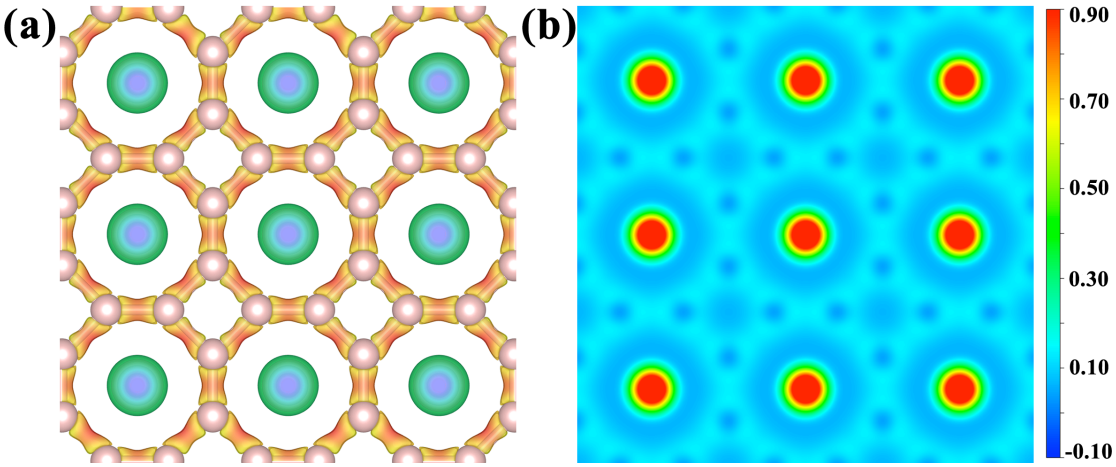

Fig. S5. Isosurfaces of deformation electronic density (DED) plotted with the value of 0.12 (a) and DED map sliced perpendicular to (001) direction (b) for the TiB_4 monolayer. In the DED maps, the red and blue color refer to the positive (0.90) and negative (-0.10) value, corresponding to electron accumulation and depletion regions, respectively.

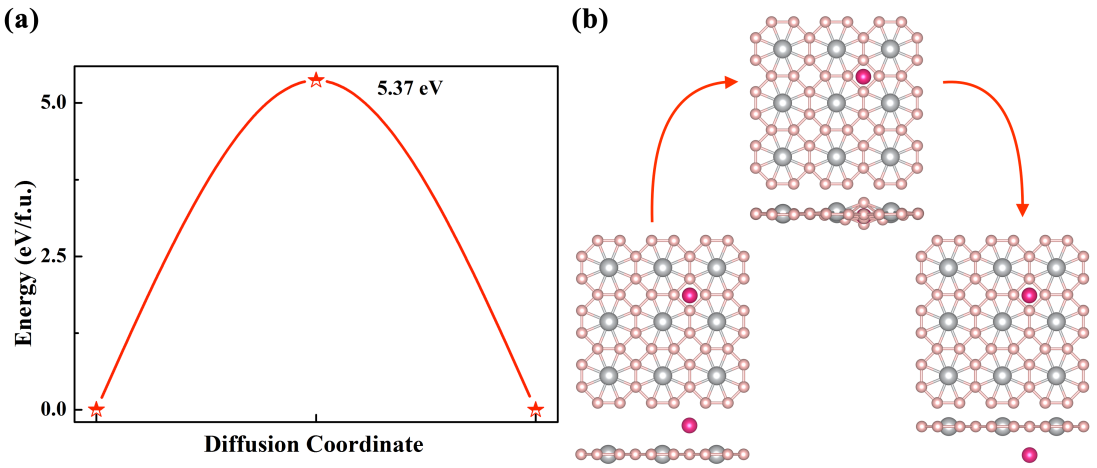

Fig. S6. Pathways for the diffusion of Li through the TiB_4 monolayer. (a) The variation of energy (red solid line) is plotted along the diffusion coordinate. The energy maximum (corresponding to the barrier value 5.37 eV) is indicated. (b) Initial, middle and final configurations of the diffusion pathway.

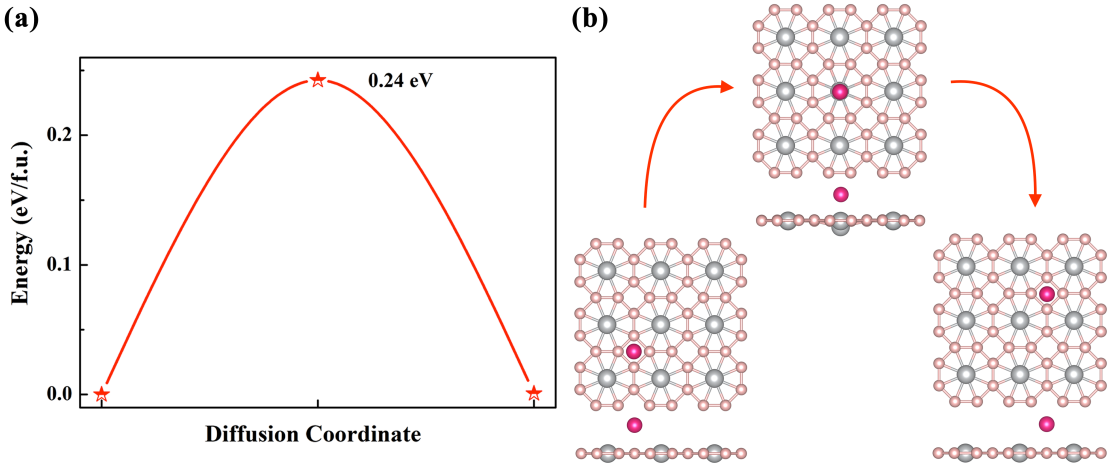

Fig. S7. Pathways for the diffusion of Li on the TiB_4 monolayer. (a) The variation of energy (red solid line) is plotted along the diffusion coordinate. The energy maximum (corresponding to the barrier value 0.24 eV) is indicated. (b) Initial, middle and final configurations of the diffusion pathway.

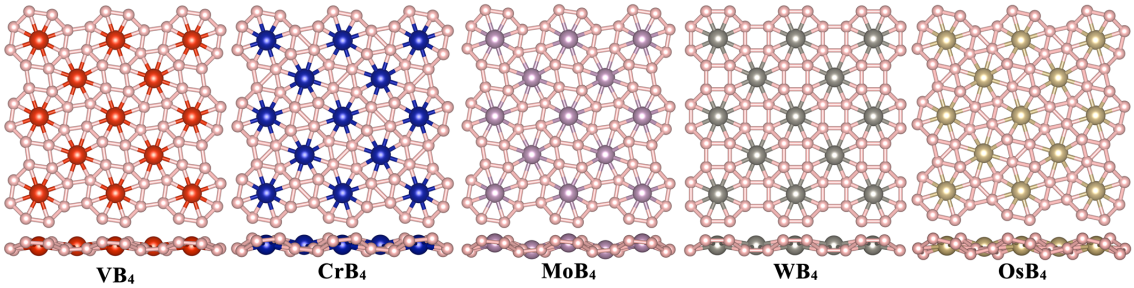

Fig. S8. Top and side views of the ball and stick model of the predicted 2D VB_4, CrB_4 MoB_4, WB_4 and OsB_4 monolayers. B atoms are denoted by pink spheres in all these structures. The transition metal atoms are located at the center of octagonal boron rings.