Supporting Information

Atomic Thin NiB$_6$ Monolayer: A Robust Dirac Material

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**Fig. S1:** Monolayer Ni$_x$B$_y$ structures searched from CALYPSO code, which are however not stable as checked from phonon calculations.
Fig. S2  Dirac cone 1 (left panel) and cone 2 (right panel) of the NiB₆ monolayer calculated using the HSE06 functional. The Fermi level is set to zero.

Fig. S3  Orbital-resolved band structures of the NiB₆ monolayer contributed by (a) $P_x$, (b) $P_y$ from the B atoms and (c) $d_{xz}$, (d) $d_{yz}$, and (e) $d_{z^2}$ from the Ni atoms. The size of the circles represent the level of contribution. The Fermi level is set to zero.
**Fig. S4** (a) Top view and side view of optimized NiB$_6$ with BN substrate. Band structures of NiB$_6$ monolayer (b) with (c) without BN substrate. The Fermi level is set to zero.

**Fig. S5** Band structures under a biaxial strain ($a$ and $b$ directions). The Fermi level is set to zero.

**Fig. S6** Band structures under a uniaxial strain ($a$ direction). The Fermi level is set to zero.
Fig. S7 Band structures under a uniaxial strain (b direction). The Fermi level is set to zero.

Detailed results from an adaptive natural density partitioning analysis are shown in Fig. S8. The first chemical bond depicts the long pairs of the d_{xz} orbital of the vertex Ni atom with ON = 1.991 |e|, compared to 2.00 |e| in the ideal case. Eight 2c-2e Ni-B σ bonds with ON = 1.991 |e| and 1.985 |e| indicate the interactions among the vertex Ni and neighboring B atoms. The additional localized 2c-2e σ bonds (ON = 1.901 |e|) is shown by two bridge B atoms between the two Ni2B4 molecular configurations. The peripheral vertex Ni atoms contribute to the Ni-B σ delocalized bonds and form four 3c-2e σ bonds with ON = 1.978 |e|. In the Ni3B4 molecule, the interaction between the two vertex Ni atoms and central B atom contribute to two 3c-2e σ bonds (ON = 1.936 |e|), while the other four 3c-2e σ bonds are formed by three B atoms with ON = 1.882 |e|. Two delocalized π bonds among the four B atoms in each Ni3B4 molecule contribute to the 4c-2e π bonds (ON = 1.924 |e|). The last two 5c-2e bonds describe the σ bonds with a low occupation number of ON = 1.907 |e|, which are mainly contributed by the 3d orbital of the Ni atom. Thus, the 2c-2e and 3c-2e σ bonds contribute to the substantial stability of the quasi-planar Ni3B8+ molecular.

Fig. S8 A chemical bonding analysis of the Ni3B8+ molecule. ON stands for the occupation number.