

Supplementary Figure 1. STM image and spectrum of DL-MoSe₂. (a) STM image of a relatively small DL-MoSe₂ on top of a large single-layer MoSe₂. (V_b =3 V, I_t =5 pA, 89 nm × 69 nm) (b) Height profile along the red dashed line in (a). The apparent heights of SL-MoSe₂ and the second layer MoSe₂ are 0.64 nm and 0.67 nm, respectively. (c) dI/dVspectrum in logarithm scale indicates the $\Delta_{\Gamma-\Gamma}$ splitting equals to 0.68 eV for the DL-MoSe₂.



Supplementary Figure 2. $(\partial Z/\partial V)_I$ spectra and statistical distributions of the Γ points. (a,b) Individual $(\partial Z/\partial V)_I$ spectra taken from MoSe₂ hole and MoSe₂ wire locations, respectively. The black arrows indicated the energy locations of the Γ points^{1,2}. (c,d) Statistical distributions for Γ points of wire and hole, respectively (based on 120 individual $(\partial Z/\partial V)_I$ spectra). $\Gamma_V^H = -2.14 \pm 0.03$ eV, $\Gamma_V^W = -2.01 \pm 0.02$ eV



Supplementary Figure 3. Projected density of states on the p orbitals of B (solid lines) and N (dotted lines) atoms in the regions indicated by the black, green, and purple circles in Figure 4a. The Fermi level is set as the zero energy.

Supplementary References

- 1. Zhang, C. et al. Probing Critical Point Energies of Transition Metal Dichalcogenides: Surprising Indirect Gap of Single Layer WSe2. *Nano Lett.* **15**, 6494-6500 (2015).
- 2. Zhang, C. et al. Visualizing band offsets and edge states in bilayer-monolayer transition metal dichalcogenides lateral heterojunction. *Nat. Commun.* **7**, 10349 (2016).