Supporting Information for

Electronic Properties of Monolayer and van der Waals Bilayer of Janus TiClI

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Calculation Methods

All the first-principles calculations were performed based on the density functional theory (DFT) as carried out in the Vienna *ab initio* Simulation Package (VASP).[1,2] In the framework of generalized gradient approximation (GGA), Perdew–Burke–Ernzerhof (PBE) was used to deal with the exchange–correlation functional.[3,4] In order to describe the electron–ion interactions, the projector augmented wave (PAW) method was adopted to resolve the DFT Kohn−Sham equations, and the cut-off kinetic energy was set to 500 eV. In order to mimic the isolated system, a vacuum space was set to 20 Å for TiClI ML and 40 Å for TiClI vdW BLs. As for geometry optimization and static electronic structure calculations, a Monkhorst–Pack k-point mesh of $11\times11\times1$ was used to sample the first Brillouin zone.[5] All structures were relaxed until the forces on each ion were less than 0.01 eV/Å^{-1}, and the energy of convergence tolerance was 10^{-6} eV

in two consecutive loops. In all calculations, SOC was considered for describing the band edge splitting. In the test calculations, three vdW dispersion corrections, DFT–D2, DFT–D3 and optB88–vdW were examined, and the total energy indicates that DFT–D2 is better for structure optimization.[6,7] In order to calculate the Berry curvature, the maximally localized Wannier function method implemented in the WANNIER90 package was employeed.[8,9]

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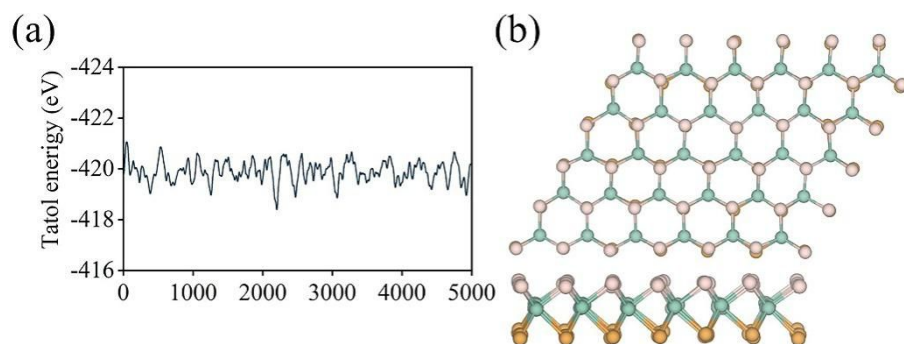
Figure S1. Variations of the (a) total energy and (b) structure for TiClI at 1000 K during AIMD calculations.
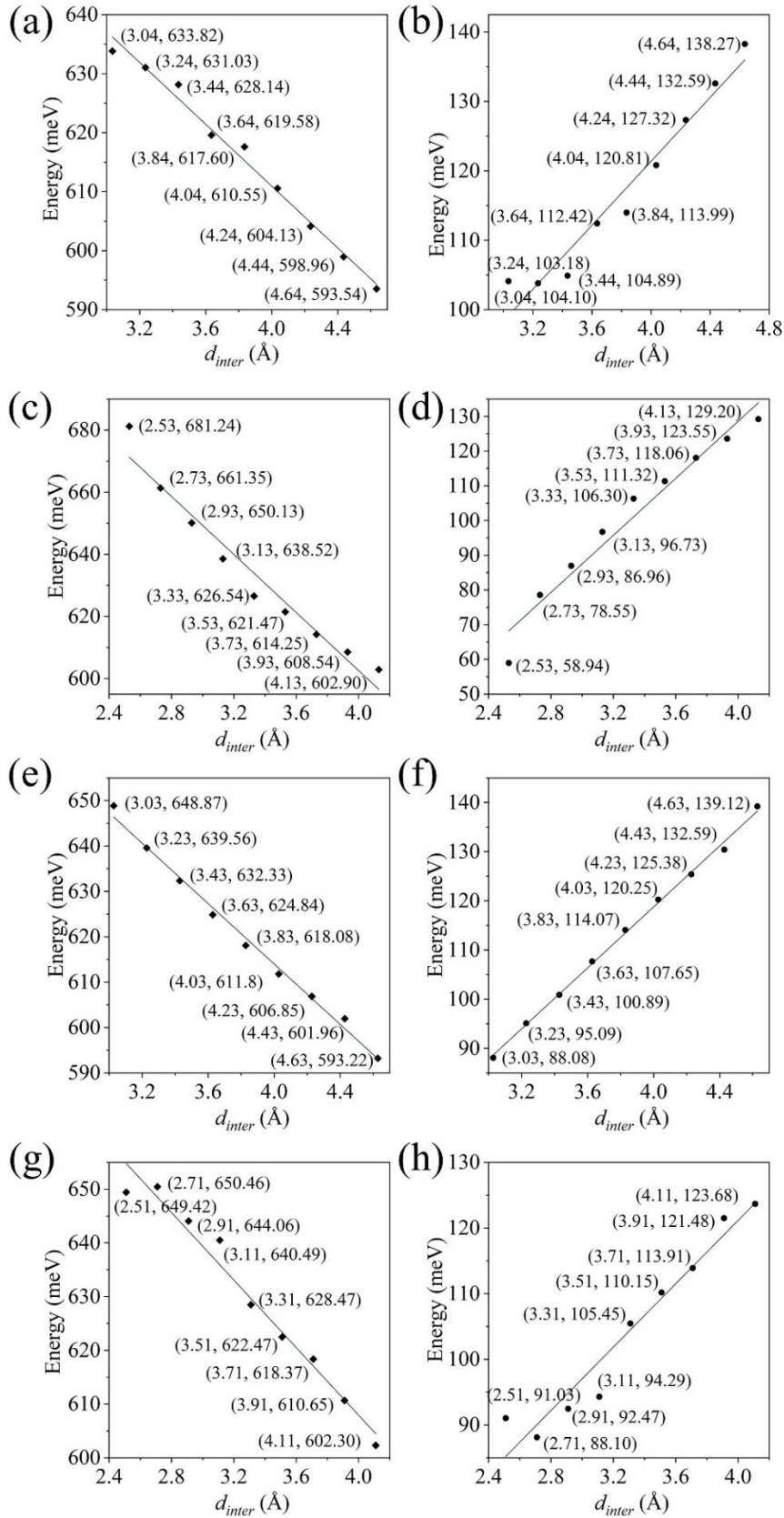
Figure S2. Variation of the band offset in the VBM and the indirect band gap with respect to the d_{inter} for TiClI vdW BLs of (a,b) AA, (c,d) AB, (e,f) A'B and (g,h) AA' stacking orders.