

Supplementary Information

N-bit Ferroelectric Tunnel Junctions via All-van-der-Waals Stacking

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S1. Structure of six two-dimensional van der Waals (2D vdW) materials

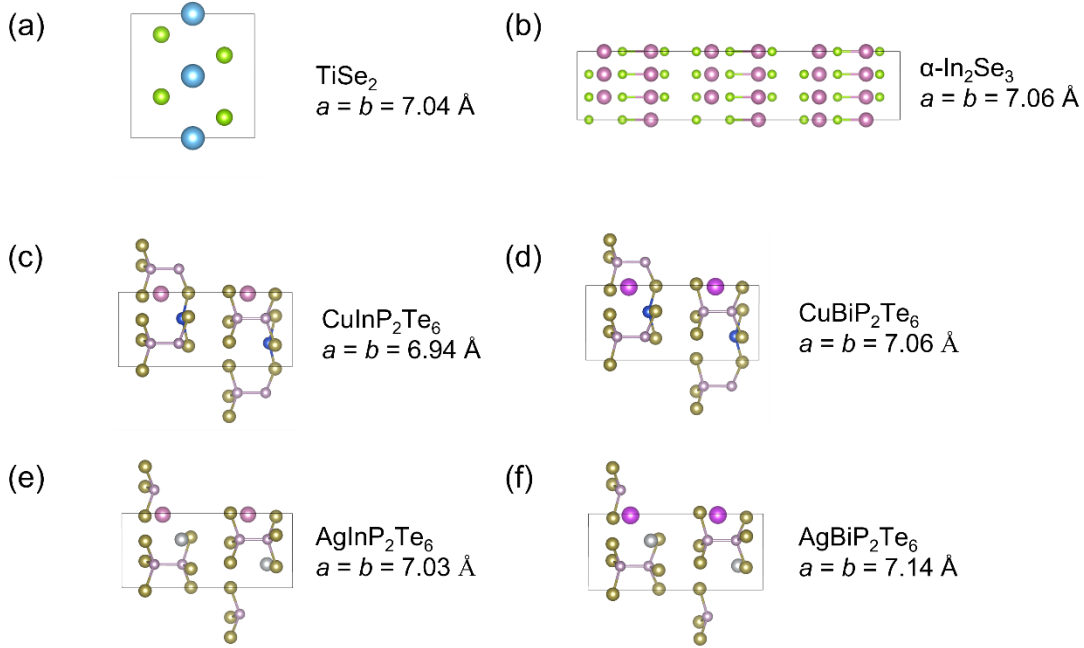


Fig. S1 Optimized structures of bulk (a) TiSe_2 , (b) $\alpha\text{-In}_2\text{Se}_3$, (c) $\text{CuInP}_2\text{Te}_6$, (d) $\text{CuBiP}_2\text{Te}_6$, (e) $\text{AgInP}_2\text{Te}_6$, and (f) $\text{AgBiP}_2\text{Te}_6$ with their lattice parameters along the a and b axes.

S2. Ferroelectric properties of four CuInP_2S_6 -family vdW materials

To validate the ferroelectric properties of the CuInP_2S_6 -family members discussed in the main text, we calculated their ferroelectric-paraelectric phase transition energy curves in Fig. S2 and their polarization values in Fig. S3. These phase transition energy curves were estimated by using the climbing-image nudged elastic band (CI-NEB) calculations,¹ and the polarization values of four ferroelectrics were calculated using the Berry phase method.²⁻⁴ The plane-wave energy cutoff was set to 400 eV, and the structural relaxations were converged with an energy threshold of 10^{-6} eV. Eight intermediate images were interpolated between the left and right ferroelectric phases to construct a possible ferroelectric-paraelectric phase transition pathway, which was subsequently refined using CI-NEB calculations. To accurately capture the quantum polarization effect, 12 linearly spaced interpolation points are generated along the ferroelectric direction for the Berry-phase spontaneous polarization calculations. The calculated energy barrier and polarization are 0.18 eV/f.u. and $4.3 \mu\text{C}/\text{cm}^2$ for $\text{CuBiP}_2\text{Te}_6$, 0.16 eV/f.u. and $2.0 \mu\text{C}/\text{cm}^2$ for $\text{CuInP}_2\text{Te}_6$, 0.15 eV/f.u. and $3.0 \mu\text{C}/\text{cm}^2$ for $\text{AgBiP}_2\text{Te}_6$, and 0.07 eV/f.u. and $0.4 \mu\text{C}/\text{cm}^2$ for $\text{AgInP}_2\text{Te}_6$ respectively.

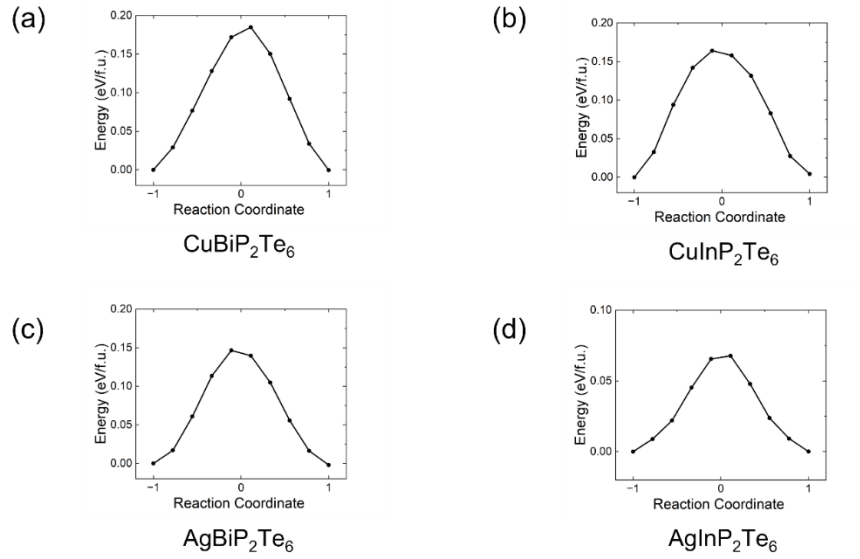


Fig. S2 Ferroelectric-paraelectric phase transition energy curves of bulk (a) $\text{CuBiP}_2\text{Te}_6$, (b) $\text{CuInP}_2\text{Te}_6$, (c) $\text{AgBiP}_2\text{Te}_6$, and (d) $\text{AgInP}_2\text{Te}_6$ based on the CI-NEB calculations. The reaction coordinate values of -1, 0, and 1 correspond to the left ferroelectric, paraelectric, and right ferroelectric phases respectively.

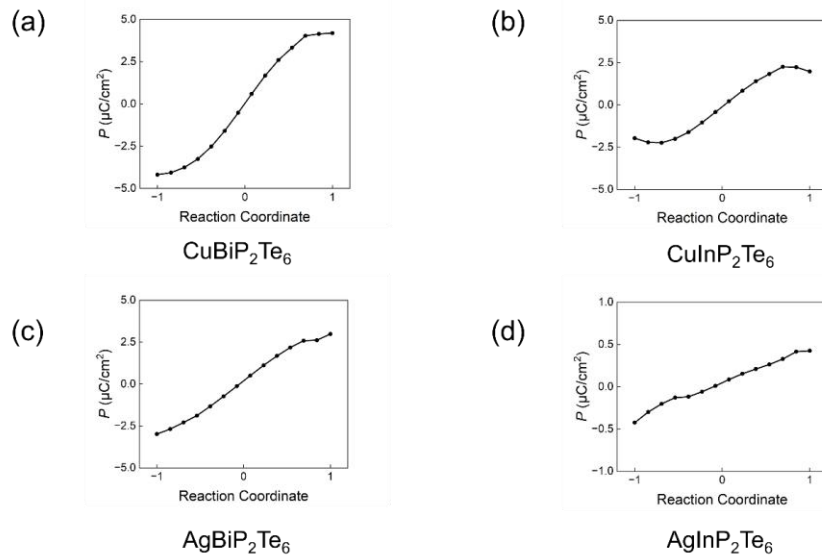


Fig. S3 Polarization curves of bulk (a) $\text{CuBiP}_2\text{Te}_6$, (b) $\text{CuInP}_2\text{Te}_6$, (c) $\text{AgBiP}_2\text{Te}_6$, and (d) $\text{AgInP}_2\text{Te}_6$ based on the Berry phase method. The reaction coordinate values of -1, 0, and 1 correspond to the left ferroelectric, paraelectric, and right ferroelectric phases respectively.

S3. Band structure of metal electrode TiSe_2

Since the metal electrode is needed for ferroelectric tunnel junctions (FTJs), we calculated band structure (Fig. S4) of TiSe_2 to prove that it is metallic without bandgap. Thus, TiSe_2 can be used as the metal electrode in our designed all-vdW FTJs.

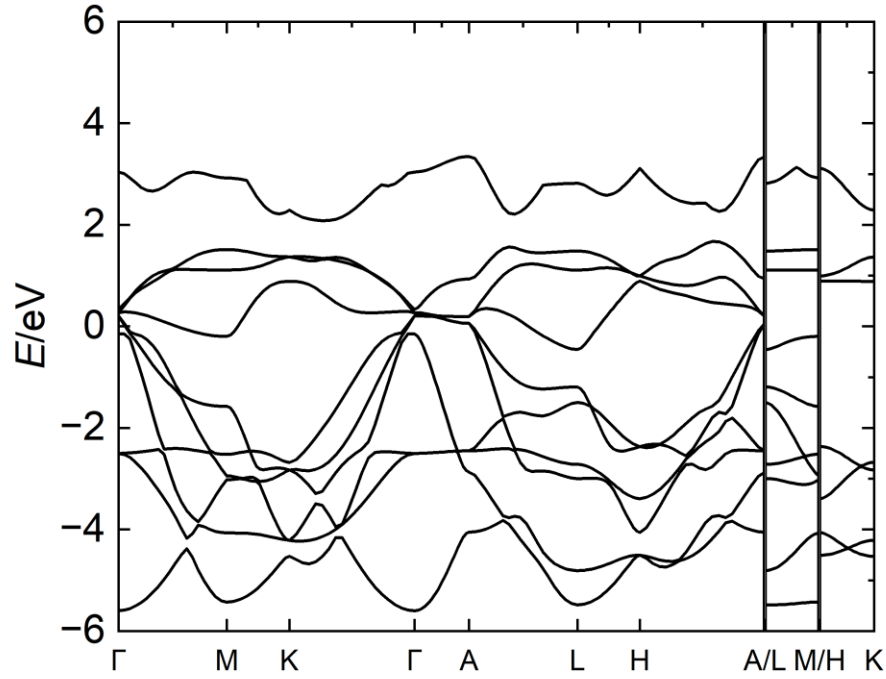
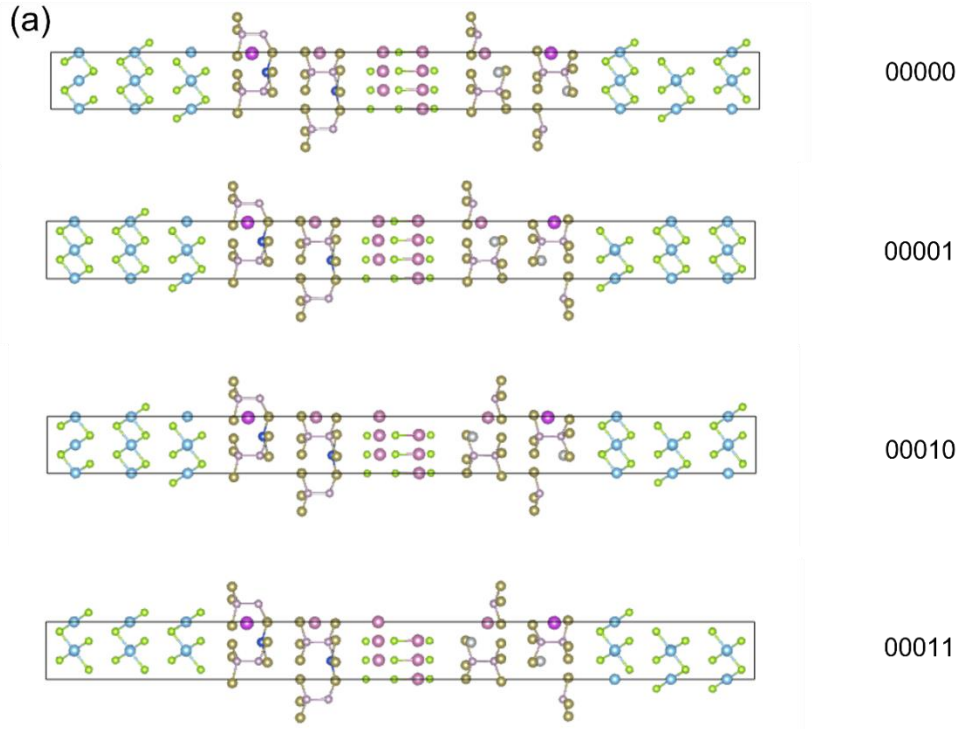


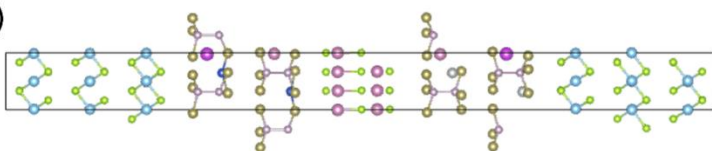
Fig. S4 Band structure of TiSe_2 .

S4. All optimized device structures of model FTJ for 32 accessible resistance states

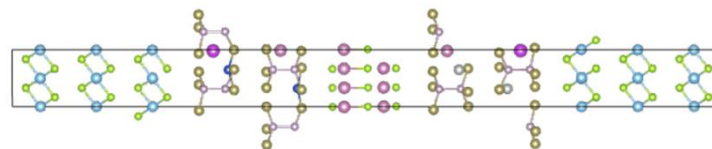
Here, we list all optimized device structures of the $\text{TiSe}_2/\text{CuBiP}_2\text{Te}_6/\text{CuInP}_2\text{Te}_6/\alpha\text{-In}_2\text{Se}_3/\text{AgInP}_2\text{Te}_6/\text{AgBiP}_2\text{Te}_6/\text{TiSe}_2$ model FTJ for 32 accessible resistance states in Fig. S5. All 32 states remain stable, each with a distinct polarization configuration.



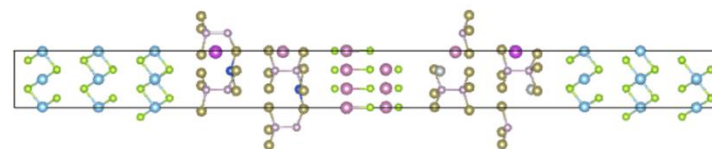
(b)



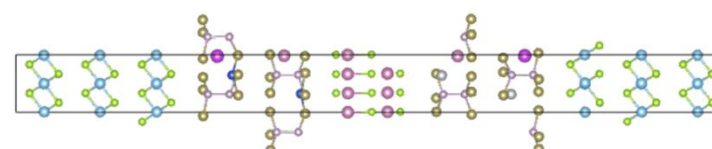
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00101

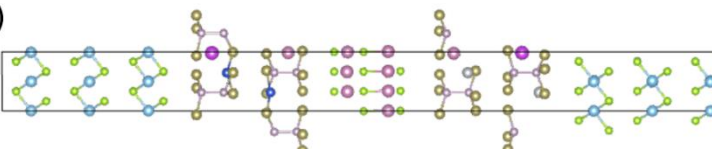


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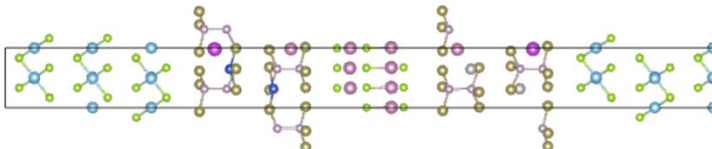


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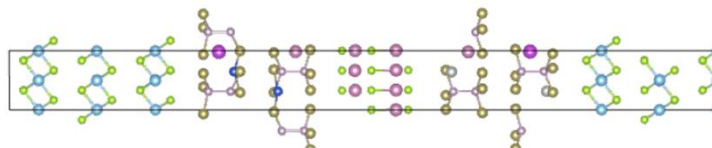
(c)



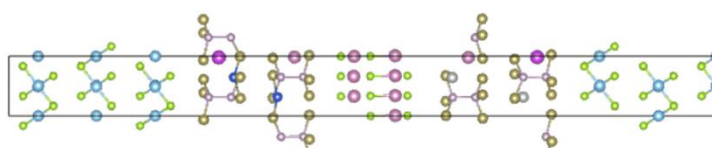
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01001

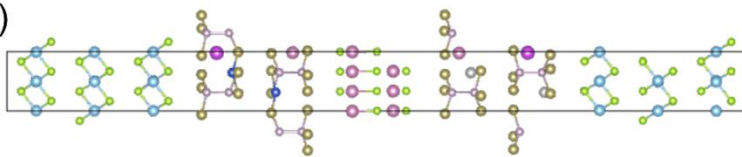


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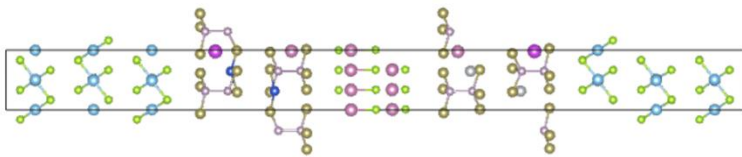


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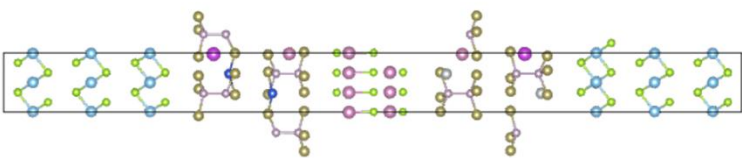
(d)



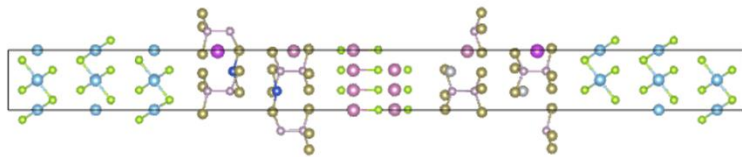
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01101

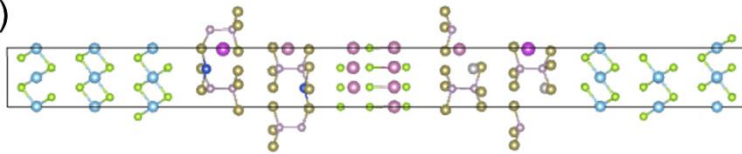


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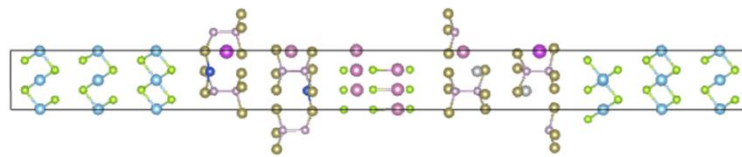


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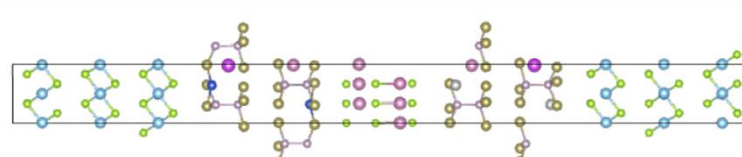
(e)



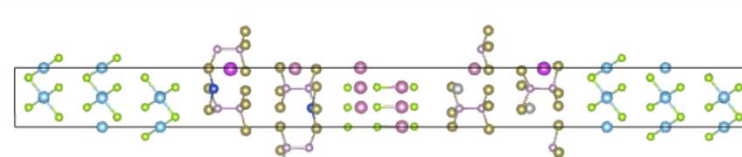
10000



10001

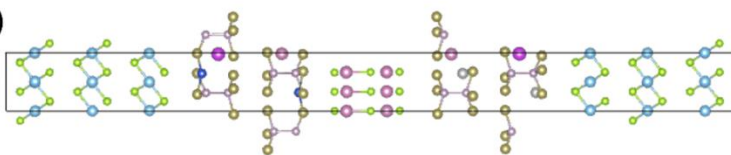


10010

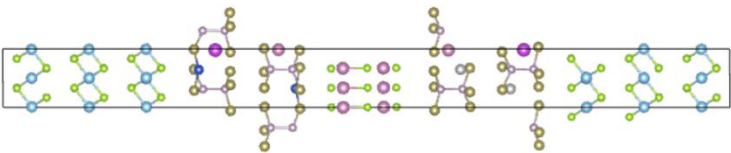


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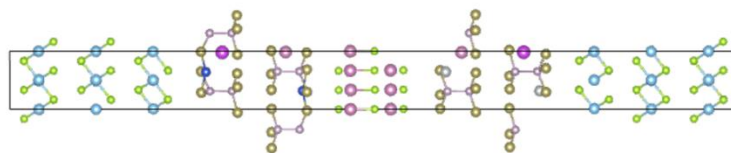
(f)



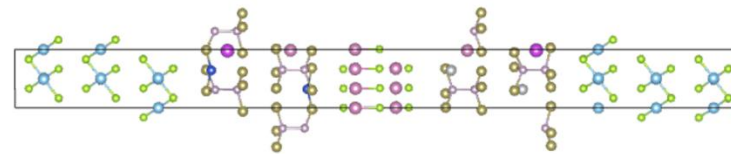
10100



10101

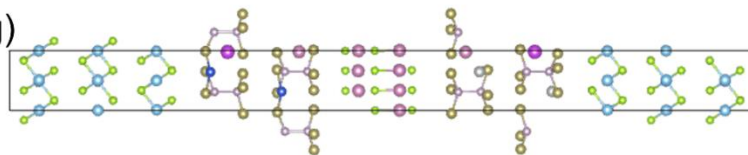


10110

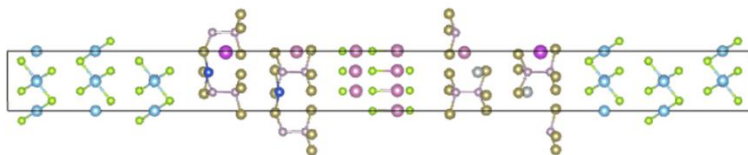


10111

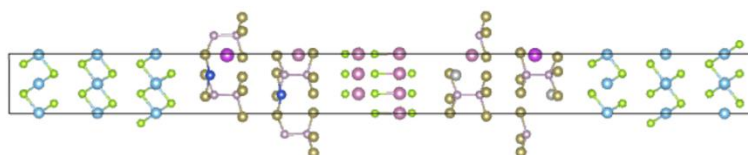
(g)



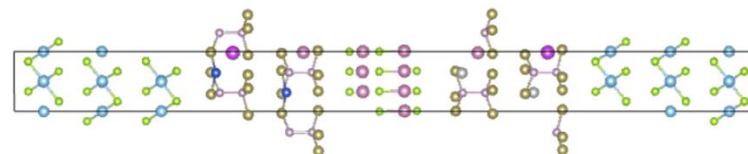
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11001



11010



11011

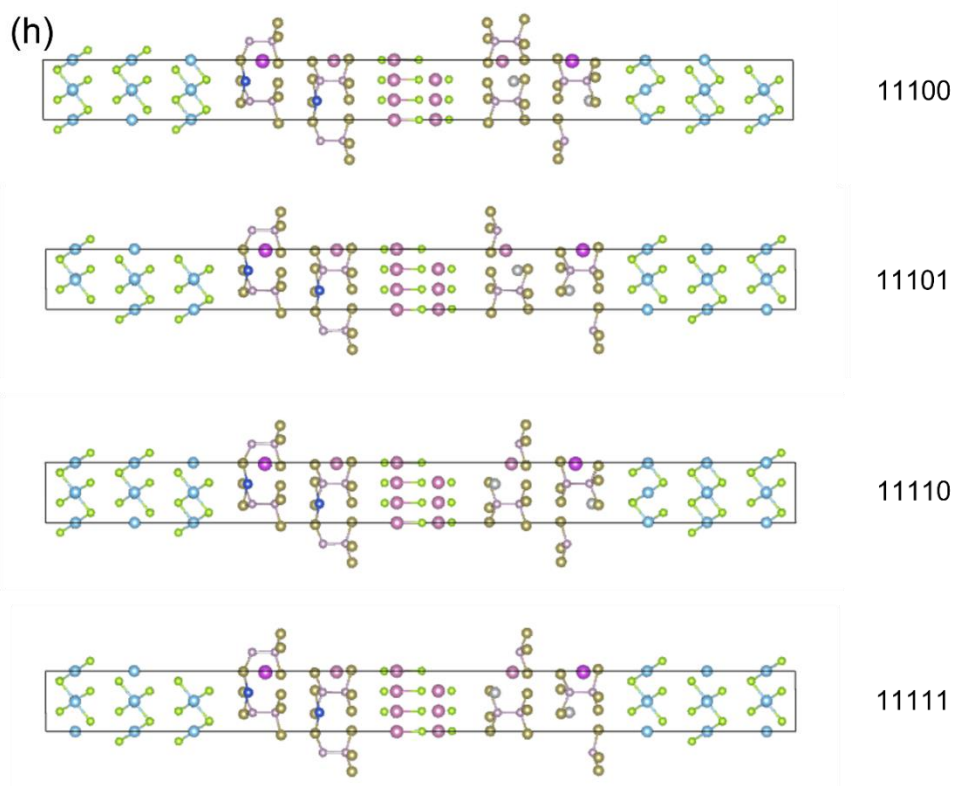


Fig. S5 Optimized device structures of model FTJ for all 32 accessible resistance states. The states are arranged in ascending binary order and grouped into panels (a)-(h), each containing four consecutive states: (a) 00000-00011, (b) 00100-00111, (c) 01000-01011, (d) 01100-01111, (e) 10000-10011, (f) 10100-10111, (g) 11000-11011, and (h) 11100-11111.

Supporting References

1. Mills, G., Jonsson, H. & Schenter, G. K. Reversible Work Transition-State Theory - Application to Dissociative Adsorption of Hydrogen. *Surf. Sci.* **324**, 305-337 (1995).
2. Kingsmith, R. D. & Vanderbilt, D. Theory of Polarization of Crystalline Solids. *Phys. Rev. B* **47**, 1651-1654 (1993).
3. Vanderbilt, D. & Kingsmith, R. D. Electric Polarization as a Bulk Quantity and Its Relation to Surface-Charge. *Phys. Rev. B* **48**, 4442-4455 (1993).
4. Resta, R. Macroscopic Polarization in Crystalline Dielectrics - the Geometric Phase Approach. *Rev. Mod. Phys.* **66**, 899-915 (1994).