

Supplementary Information for **Multi-state Data Storage in a Two-dimensional Stripy Antiferromagnet Implemented by Magnetoelectric Effect**

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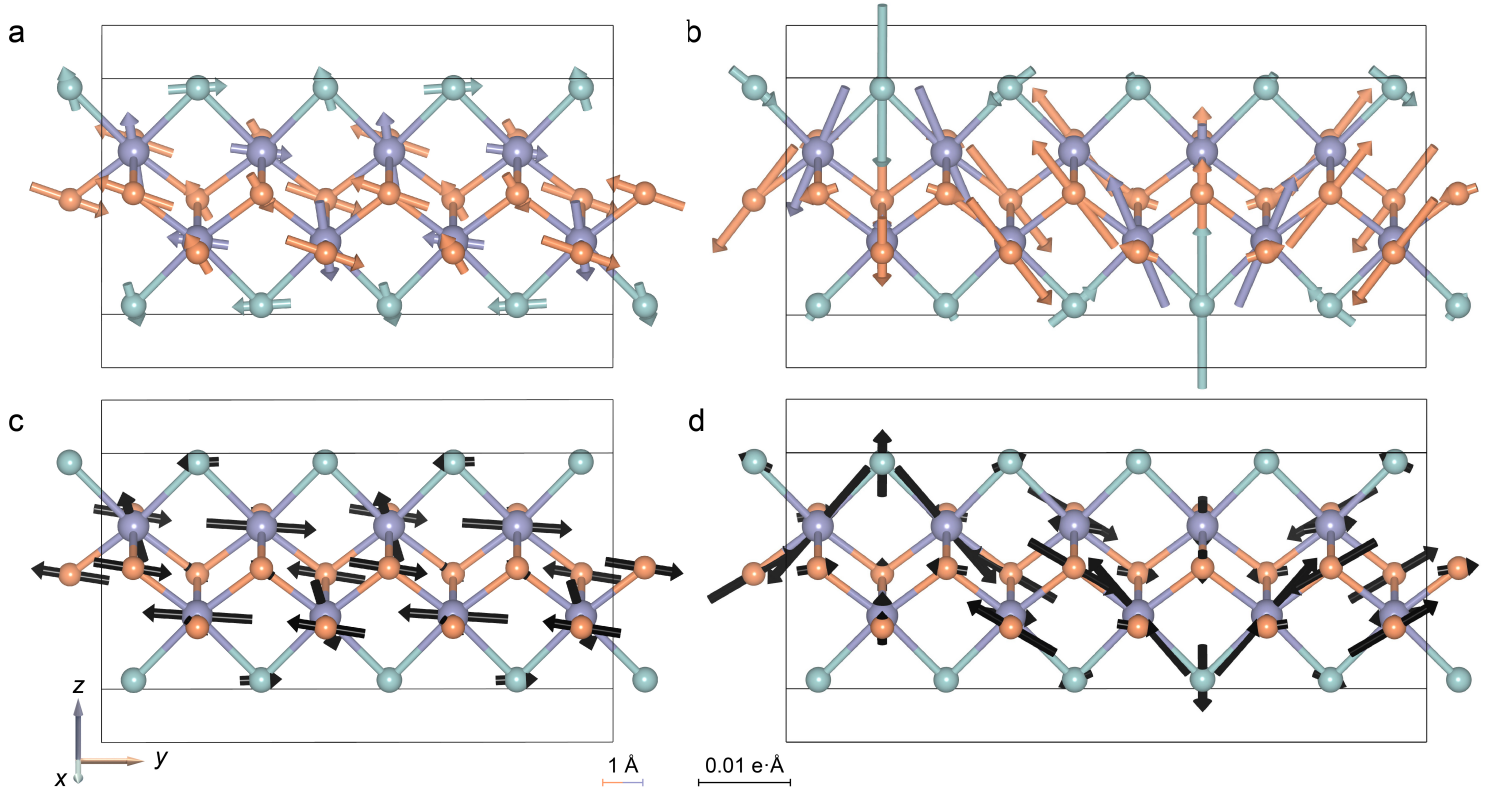


Fig. S1 Atomic displacements and dipoles of CrOCl. (a, b), The atomic distortion configurations of CrOCl in the $\uparrow\uparrow\downarrow\downarrow$ (a) and the $\uparrow\uparrow\uparrow\downarrow\downarrow$ (b) phases. The vectors on each atom represent the atomic displacements which are magnified 100 times. (c, d), The dipole configurations of CrOCl in the $\uparrow\uparrow\downarrow\downarrow$ (c) and the $\uparrow\uparrow\uparrow\downarrow\downarrow$ (d) phases. Black arrows depict theoretical predictions of the electric polarization of each atom by the Born effective charge method. The scale bars of the Cartesian coordinates and the electric dipoles are plotted at the bottom.

Table S1 Calculated space group, lattice parameters and net electric dipole under the external electric field in the $\uparrow\uparrow\downarrow\downarrow$ and $\uparrow\uparrow\uparrow\downarrow\downarrow$ phases of CrOCl. The electric dipole was obtained under an external field of 0.07 V/Å along the +z-direction in a single unit cell.

	$\uparrow\uparrow\downarrow\downarrow$	$\uparrow\uparrow\uparrow\downarrow\downarrow$
Structure	Monoclinic $P2_1/m$	Orthorhombic $Pmmm$
Unit cell	(a, 4b c)	(a, 5b, c)
a (Å)	3.89413	3.89458
b (Å)	3.19511	3.19648
c (Å)	7.67976	7.67714
α (°)	90.0627	90.0000
V (Å ³)	382.211636	477.861592
P (e·Å)	0.00278	0.00043

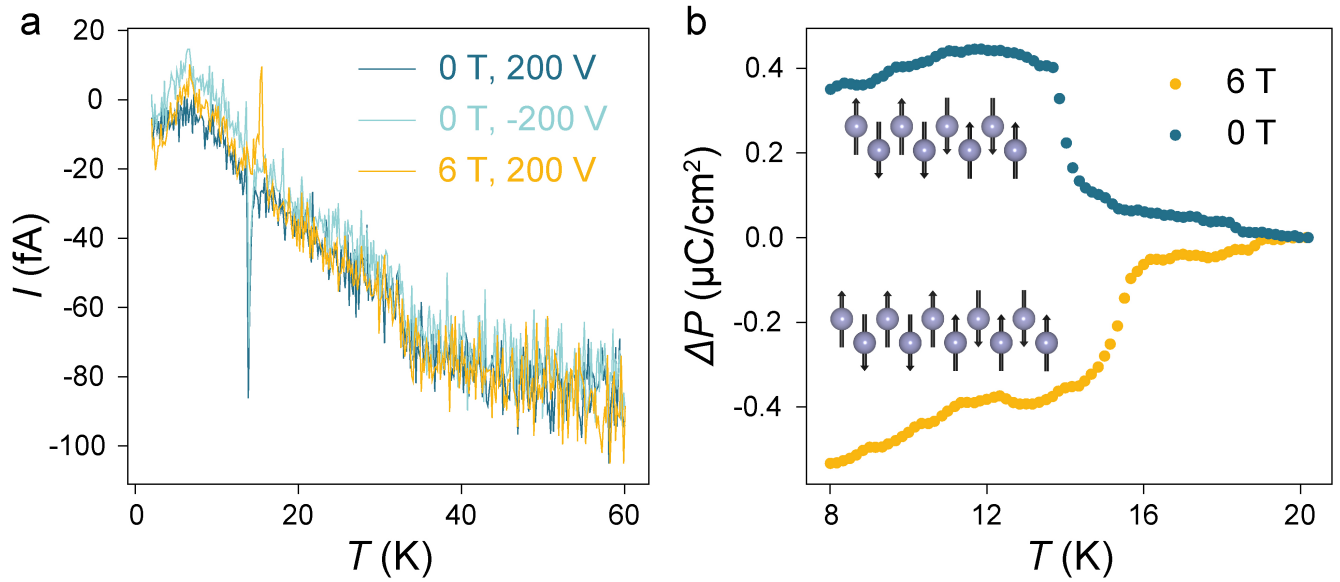


Fig. S2 Temperature-dependent polarization of CrOCl crystals. (a), Pyroelectric current *versus* temperature under external fields of 0 T and 6 T with a poling voltage of ± 200 V. The current peaks at the magnetic transition temperatures and does not respond to the varying poling voltage, but changes sign under the external field. (b), Temperature dependence of the electric polarization ΔP under magnetic fields of 0 T and 6 T obtained by integrating the current over time. The corresponding spin configurations are illustrated in the insets. The electric polarization of the $\uparrow\uparrow\downarrow\downarrow$ phase is parallel to the applied field, while that of $\uparrow\uparrow\downarrow\uparrow$ phase is antiparallel to the applied electric field. Both critical temperatures agree well with the magnetic phase diagram of CrOCl¹. Considering the fact that ϵ_r does not exhibit divergent behavior at the transition temperatures (Fig. 1c in the main text) and the polarization cannot be switched by the poling field, we rule out the possibility of spontaneous ferroelectric polarization. The pyroelectric current of CrOCl probably originates from uncompensated antiferroelectric domains.

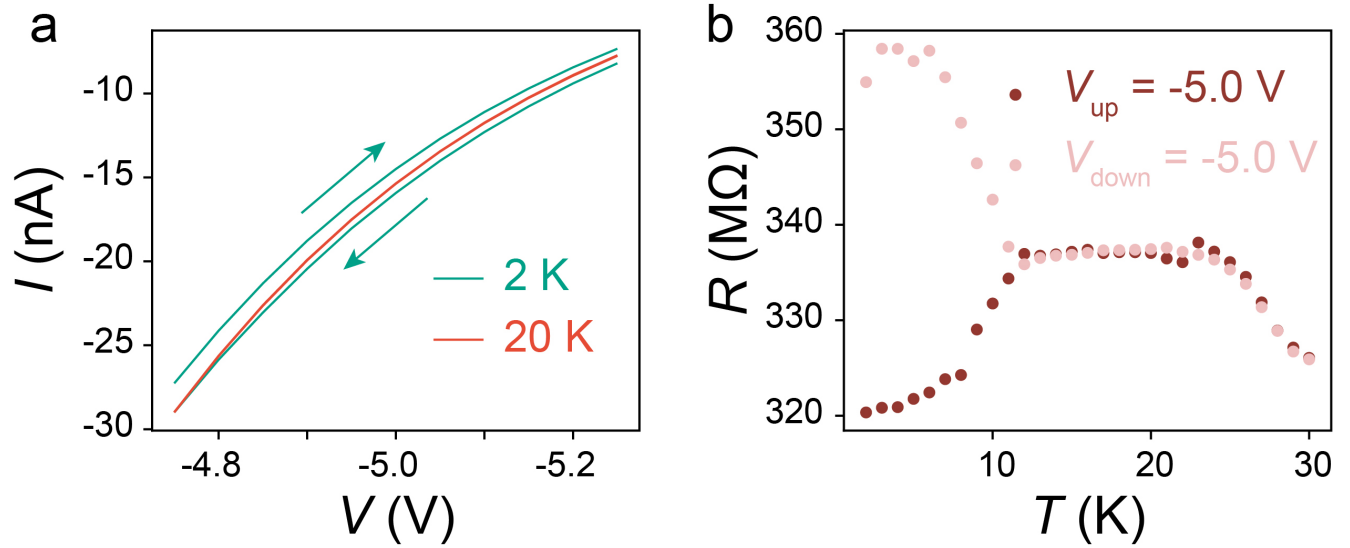


Fig. S3 Hysteresis behavior at negative voltages. (a), $I - V$ curves of the CrOCl tunneling device at 20 K (above the Néel temperature) and 2 K (below the Néel temperature). (b), Resistance *versus* temperature of the CrOCl tunneling device at -5 V in different sweeping processes. Data are collected from the same device as Fig. 2 in the main text.

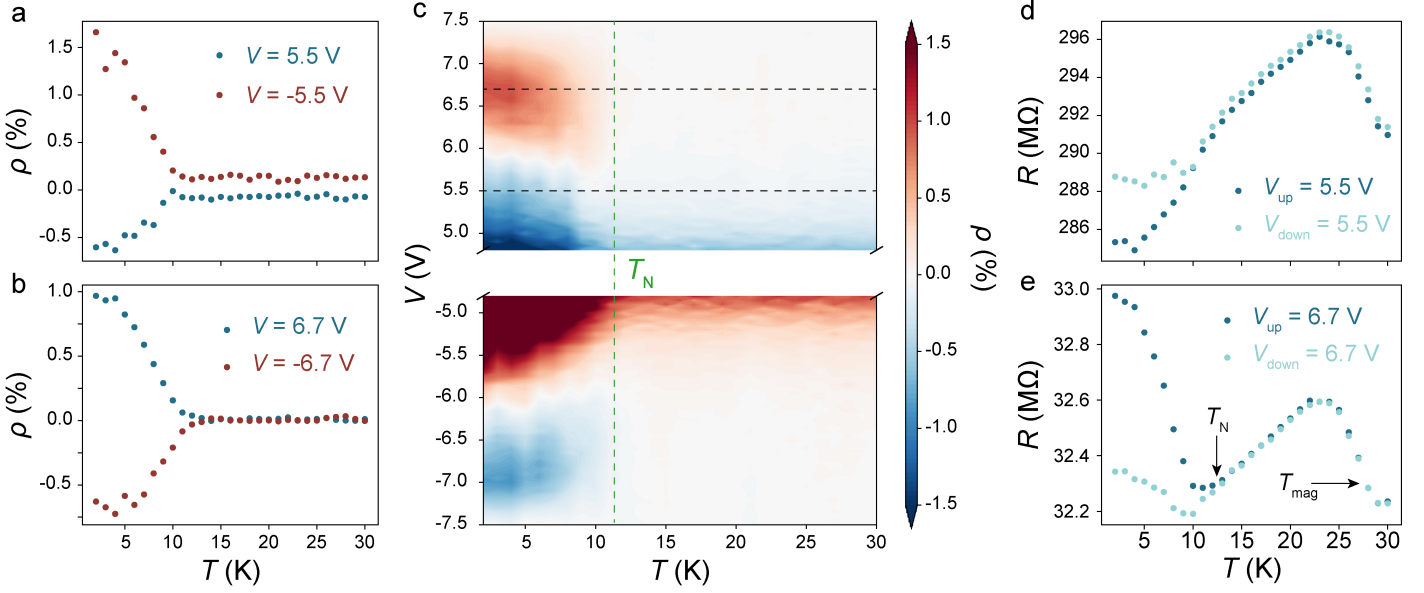


Fig. S4 $I - V$ hysteresis of a 10-nm CrOCl tunneling device below Néel temperature. (a,b), Current polarization $\rho = (R_{up} - R_{down}) / (R_{up} + R_{down})$ versus temperature at ± 5.5 V (a) and ± 6.7 V (b). (c), 2D map of current polarization ρ as a function of temperature and bias voltage. The vertical green dashed line marks the Néel temperature of the exfoliated CrOCl. The horizontal black dashed lines mark the bias voltages of 5.5 V and 6.7 V. (d,e), Resistance versus temperature of the CrOCl tunneling device at 5.5 V (d) and 6.7 V (e) in different sweeping processes.

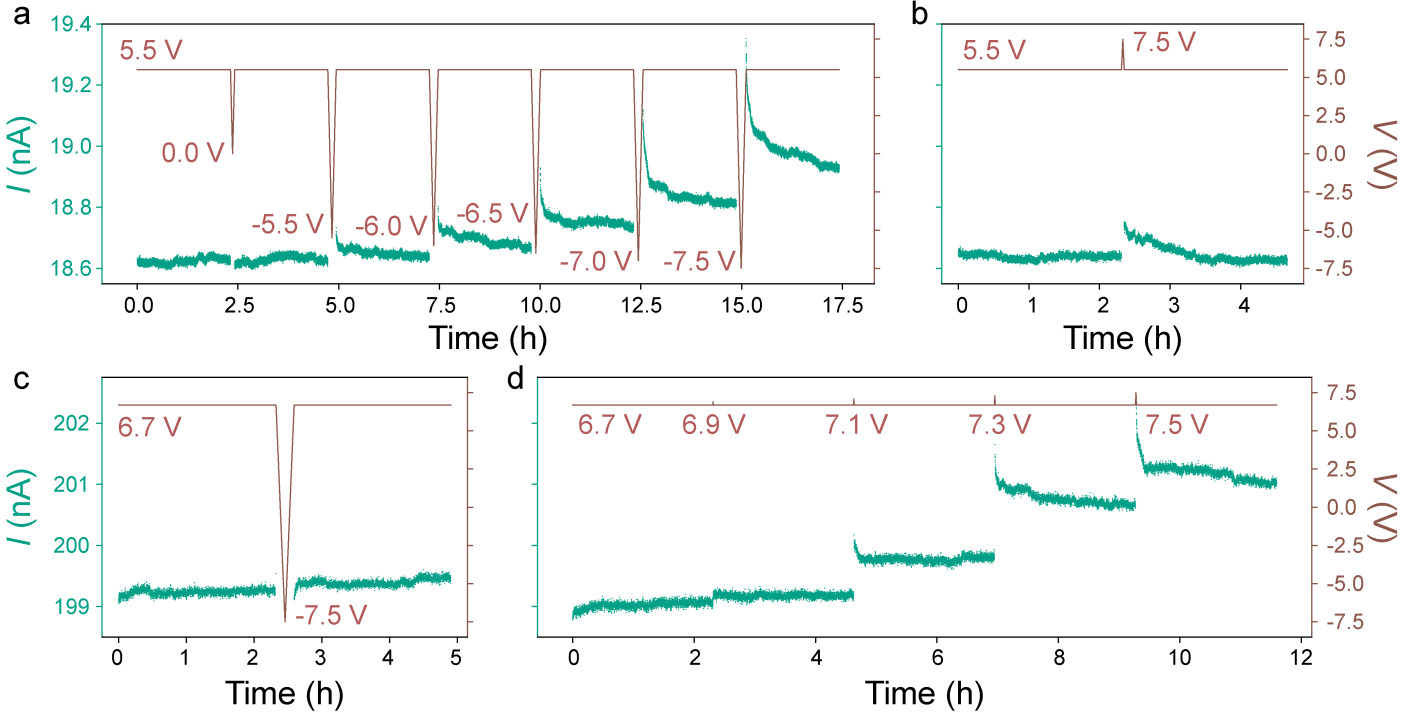


Fig. S5 Tunneling current relaxation process at different voltages of the 10-nm tunneling device. (a,b), Time-dependent relaxation curves at 5.5 V after downward (a) and upward (b) triangular pulses. (c,d), Time-dependent relaxation curves at 6.7 V after downward (c) and upward (d) triangular pulses.

In the following, we discuss the origin of hysteresis loops in tunneling devices. Surprisingly, the $I - V$ hysteresis of CrOCl exhibits an inversion at the bias voltage of ~ 6 V, from the clockwise hysteresis at low voltages to the counterclockwise hysteresis at high voltages, as shown in Fig. S4c. Although both hysteresis regions (above and below 6 V) are closely related to the appearance of electric dipoles below the Néel temperature, they may be attributed to different mechanisms. As revealed by the relaxation curves in Fig. S5a-b, in the clockwise hysteresis region, the sweep-up processes (from a lower voltage to 5.5 V) excite the device to high-current states followed by slow relaxation, while the sweep-down (from a higher voltage to 5.5 V) process shows no obvious effect. In other words, the clockwise hysteresis is completely caused by the excitation of the sweeping field, which tilts the electric dipoles toward the field direction and gives rise to a higher current. However, the $\uparrow\uparrow\downarrow$ stripy AFM order tends to settle the system to the antiferroelectric state in the presence of ME coupling, thus resulting in the slow relaxation process.

Naturally, the current states would be highly correlated with the response of the electric dipoles to the external field. We speculate that over 6 V, CrOCl transforms to a new ground state, resembling the $\uparrow\uparrow\downarrow\downarrow$ state under magnetic field. The sweep-up processes can no longer tilt the dipole moments as the paraelectric phase below 6 V. Instead, a larger inverse field will be needed to overcome the potential barrier to transforming the device to the ground antiferroelectric state, as shown in Fig. S5c-d. In other words, the anticlockwise hysteresis over 6 V is a consequence of $P - E$ hysteresis of a first-order structural transition.

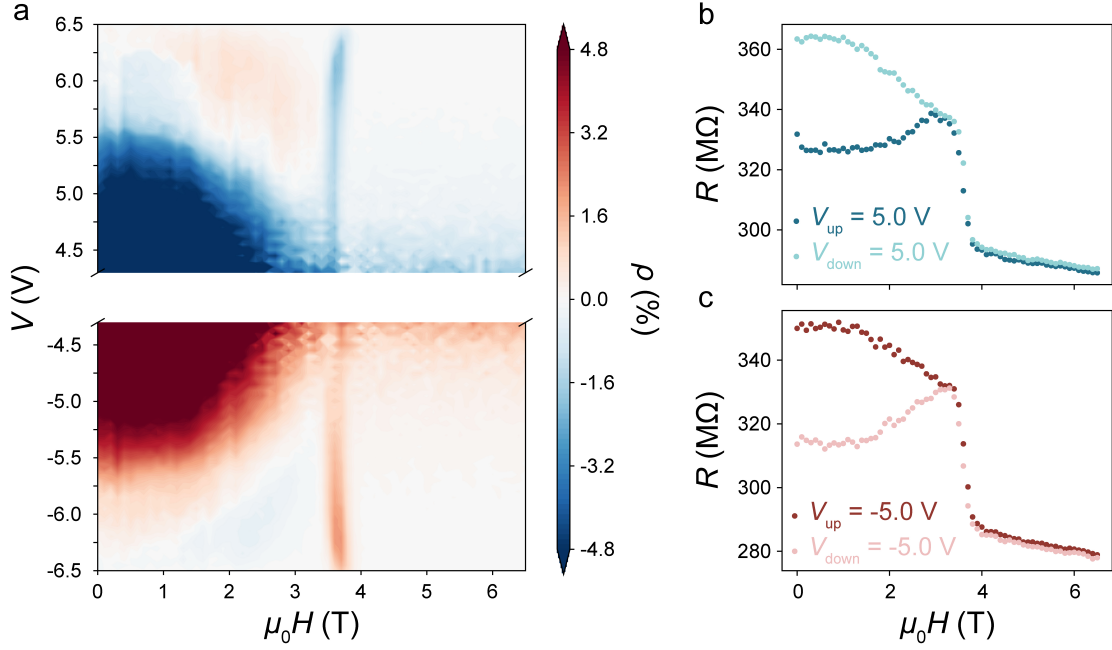


Fig. S6 $I - V$ hysteresis of a 10-nm CrOCl tunneling device at 2 K under out-of-plane external field. (a), 2D map of current polarization ρ as a function of out-of-plane magnetic field and bias voltage. (b,c), Tunneling resistance *versus* out-of-plane magnetic field at 5.0 V (b) and -5.0 V (c) in different sweeping processes.

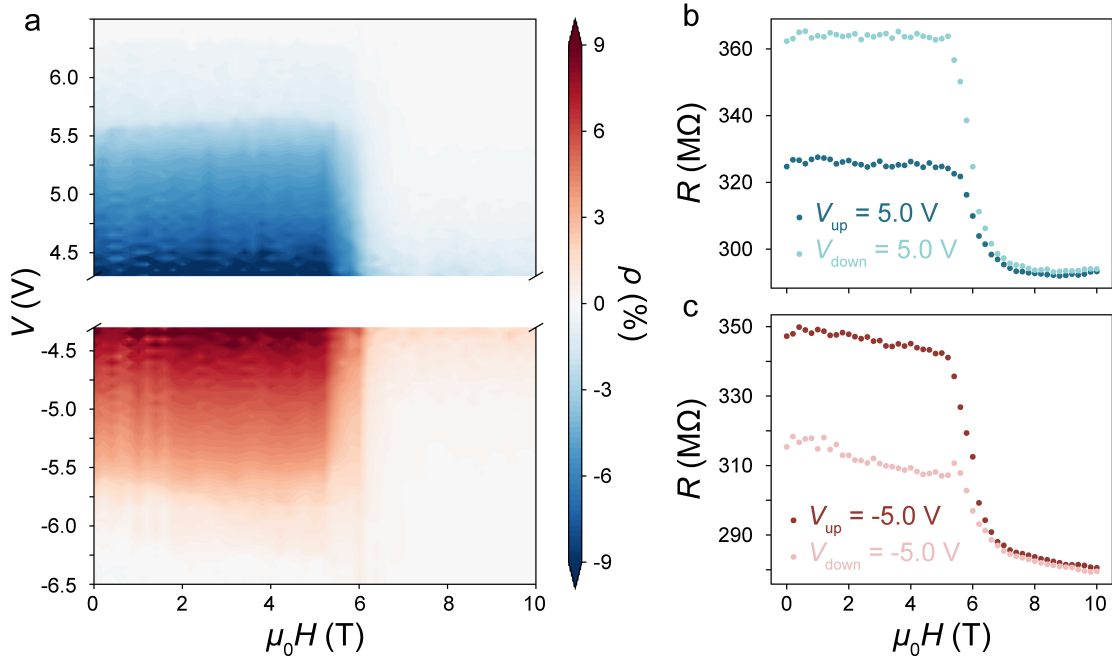


Fig. S7 $I - V$ hysteresis of a 10-nm CrOCl tunneling device at 2 K under in-plane external field. (a), 2D map of current polarization ρ as a function of in-plane magnetic field and bias voltage. (b,c), Tunneling resistance *versus* in-plane magnetic field at 5.0 V (b) and -5.0 V (c) in different sweeping processes.

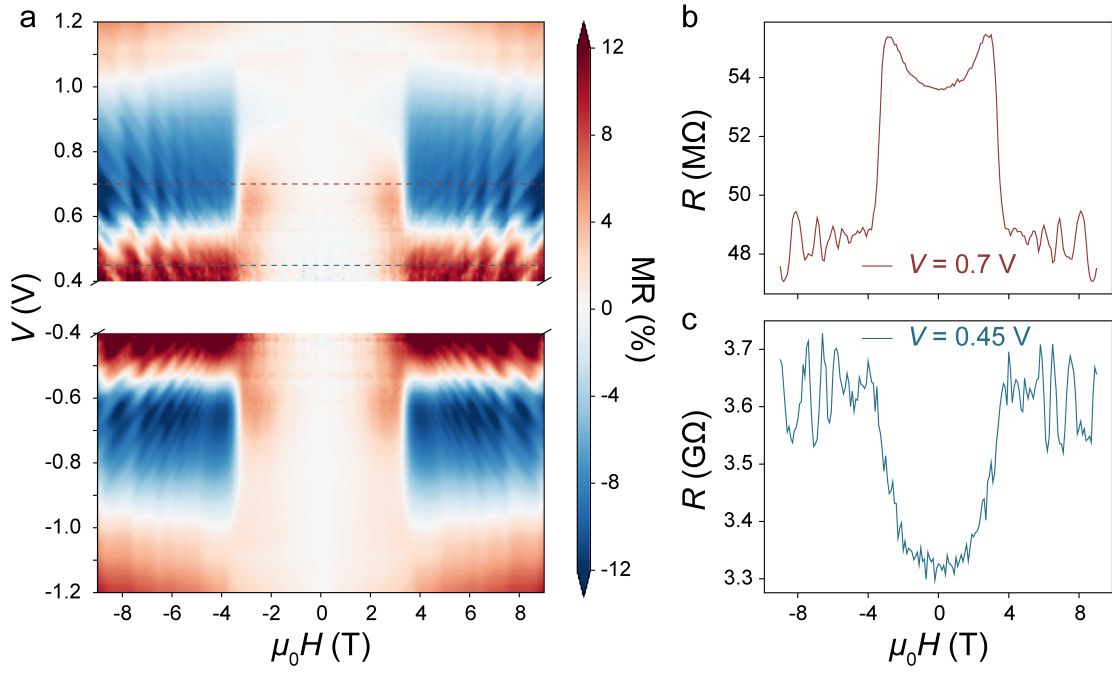


Fig. S8 Symmetric magnetoresistance (MR) behavior of a 4-L tunneling device. (a), 2D map of magnetoresistance $MR = (R(B) - R(0 T)) / R(0 T)$ as a function of out-of-plane magnetic field and bias voltage. The horizontal dashed lines mark the bias voltage of 0.7 V and 0.45 V. (b,c), The resistance *versus* out-of-plane magnetic field of the CrOCl tunneling device at 0.7 V (b) and 0.45 V (c) extracted from the dashed lines in (a). The change in magnetoresistance at different voltages is direct evidence of electrically driven phase transitions. As pointed out earlier, the electric dipoles in the $\uparrow\uparrow\downarrow\downarrow$ phase can be tilted by the electric field, while the $\uparrow\uparrow\downarrow\downarrow$ is rather immune to the external electric field. As a result, the tunneling barrier difference between the two phases varies with the bias voltage, leading to opposite magnetoresistance behaviors at different voltages.

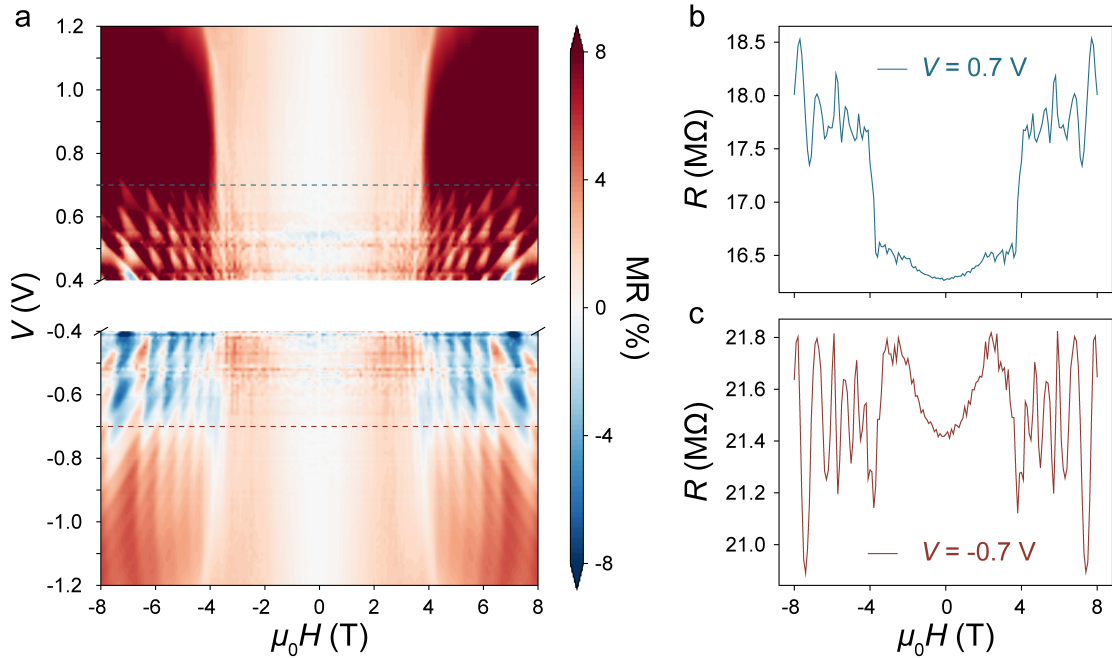


Fig. S9 Asymmetric magnetoresistance (MR) behavior of a 4-L tunneling device. (a), 2D map of MR as a function of out-of-plane magnetic field and bias voltage. (b,c), The resistance *versus* out-of-plane magnetic field of the CrOCl tunneling device at 0.7 V (b) and -0.7 V (c) extracted from the dashed lines in (a). The asymmetric magnetoresistance on positive and negative voltages is probably resulted from the asymmetry of graphite contacts. Few-layer graphite flakes usually possess finite density of states and cannot completely screen the interface charges as ideal metals. Incomplete screening gives rise to an additional electrostatic potential at the barrier/graphite interface (> 0 when P points towards the interface and < 0 when P points away from the interface)²⁻⁴. Consequently, if the graphite contacts at the two sides of CrOCl are highly asymmetrical, they will produce different additional potential barriers under positive and negative voltages, respectively. A lower additional barrier should result in positive magnetoresistance (b), while a higher additional barrier should result in negative magnetoresistance (c).

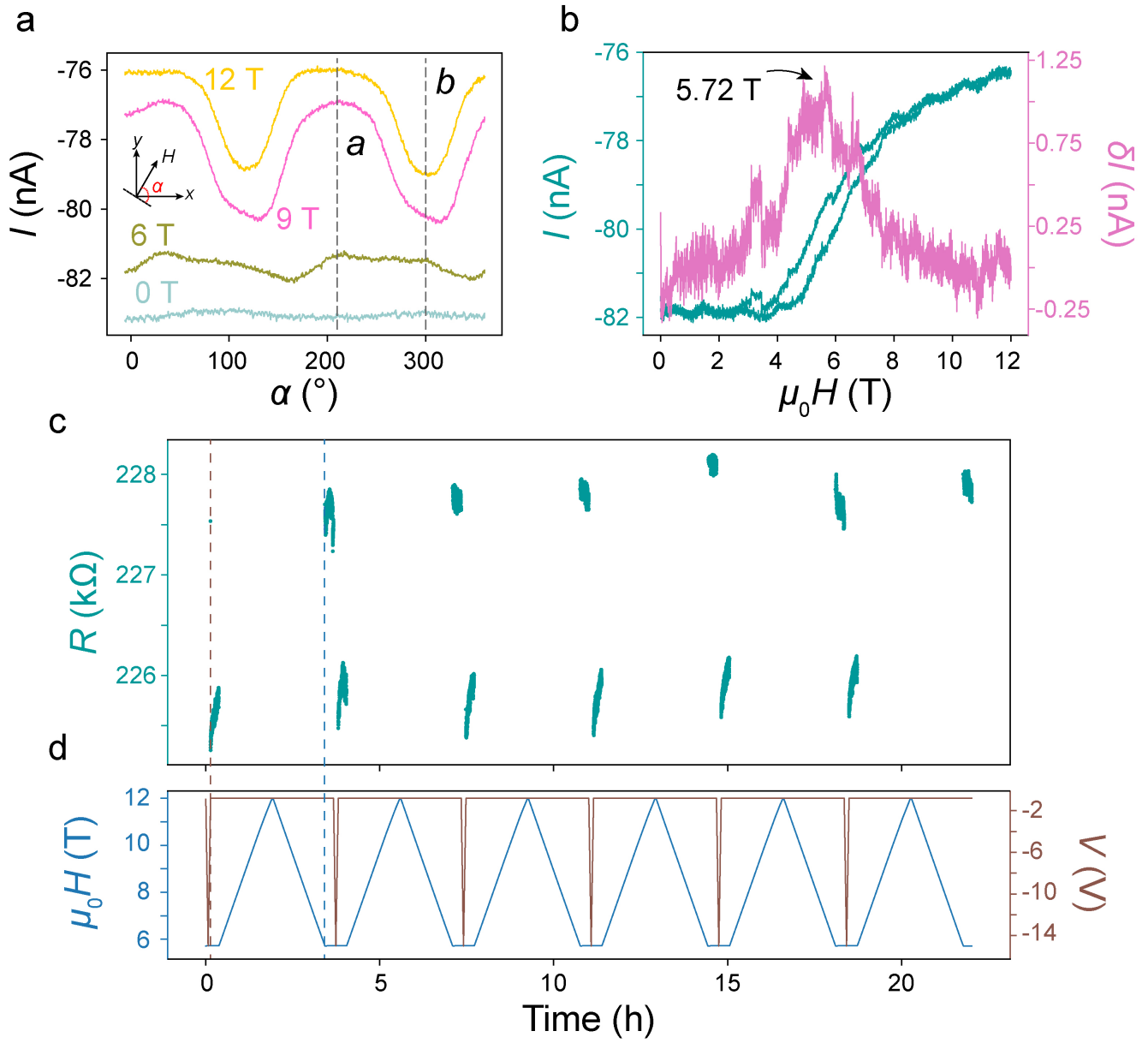


Fig. S10 Magnetoelectric coupling in a single-layer CrOCl tunneling device. (a), Tunneling current of the single-layer device on the dependence of the in-plane field direction at different magnetic magnitudes. (b), $I - B$ curve of the CrOCl tunneling device at 2 K with the external field along with the a -axis. The pink curve shows the differential current $\delta I = I(B_{\text{down}}) - I(B_{\text{up}})$. The critical field where δI reaches a maximum is annotated by the black arrow. (c,d), Tunneling current (c) after alternating electric and magnetic excitations. The corresponding magnetic and electric fields *versus* time are plotted in (d). The device was parallel-connected with a 10 MΩ protection resistor.

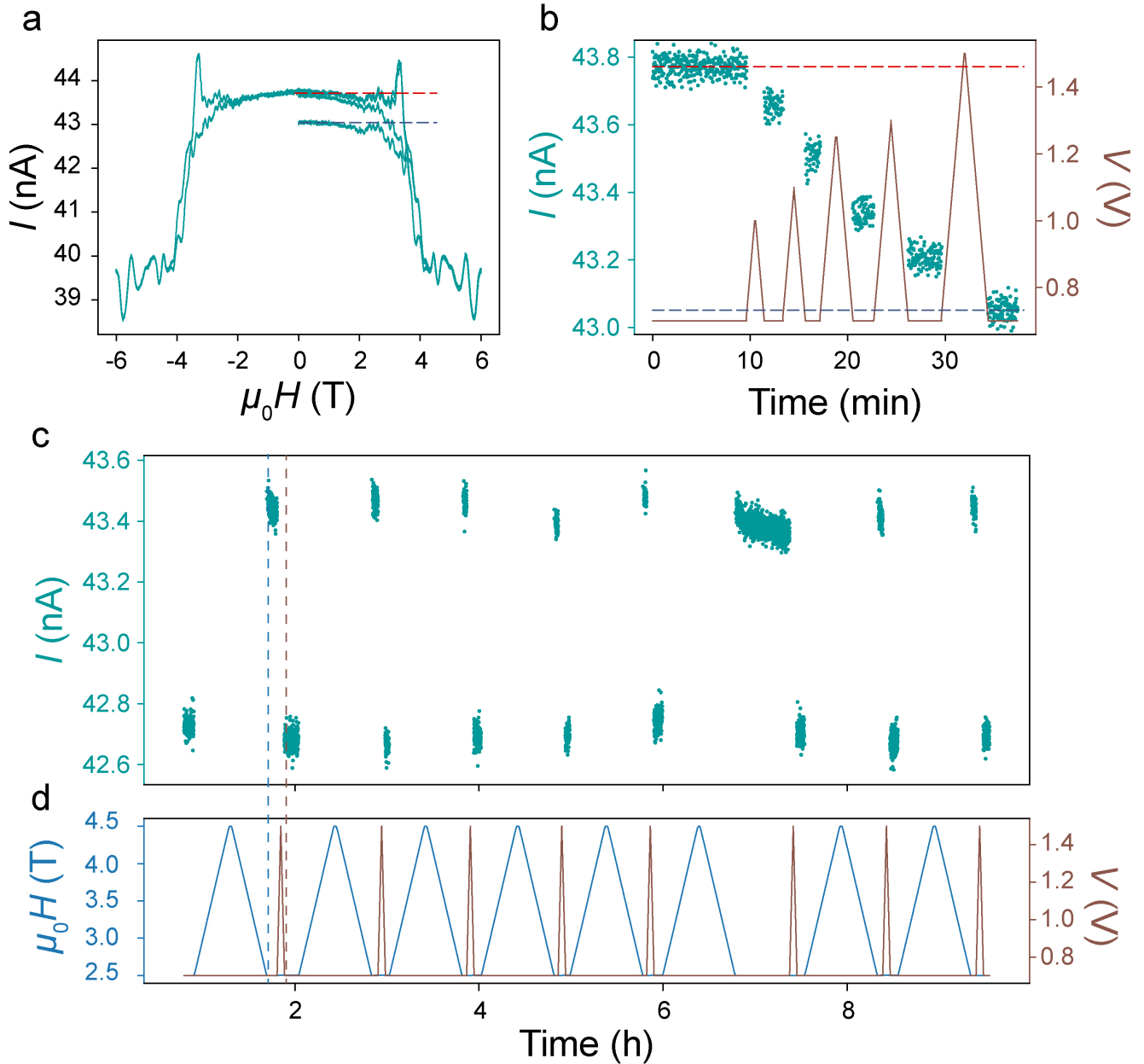


Fig. S11 Magnetoelectric coupling at zero magnetic field in a 4-L CrOCl tunneling device. (a), $I - B$ curve of the CrOCl tunneling device at 2 K. After sweeping back to zero field from a large out-of-plane magnetic field (larger than B_s), the device reaches a high-current excited state (red dashed line) at zero field. The new state should be another metastable state in the $\uparrow\uparrow\downarrow\downarrow$ phase, which is achieved after a series of structural transitions accompanied with the magnetic transitions. (b), Tunneling current over time after each electric excitation at zero magnetic field. The red and blue dashed lines represent the current values of the excited state and the ground state at 0 T extracted from (a), respectively. (c,d), Tunneling current (c) after alternating electric and magnetic excitations. The corresponding magnetic and electric field *versus* time are plotted in (d). The initial field is set to 2.5 T for a lower magnetic excitation, which does not affect the current states substantially.

References

- [1] Gu, P. *et al.* Magnetic phase transitions and magnetoelastic coupling in a two-dimensional stripy antiferromagnet. *Nano Lett.* (2022).
- [2] Garcia, V. & Bibes, M. Ferroelectric tunnel junctions for information storage and processing. *Nat. Commun.* **5**, 1–12 (2014).
- [3] Zhuravlev, M. Y., Sabirianov, R. F., Jaswal, S. & Tsymbal, E. Y. Giant electroresistance in ferroelectric tunnel junctions. *Phys. Rev. Lett.* **94**, 246802 (2005).
- [4] Kohlstedt, H., Pertsev, N., Contreras, J. R. & Waser, R. Theoretical current-voltage characteristics of ferroelectric tunnel junctions. *Phys. Rev. B* **72**, 125341 (2005).