

Supporting Information for Observation of field-odd and field-free superconducting diode effects in Mo₂C nanoflakes

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1 Measurement of critical currents from adjacent microstrips

Because we design orthogonal microstrips that are connected end-to-end, we can measure them jointly to save measurement time. In this configuration, we pass a shared current, which includes a DC bias and an AC excitation, through the L-shaped channel containing two adjacent microstrips, and we monitor the voltages of individual segments simultaneously. However, such a measurement scheme creates a severe problem where the critical currents of both channels always appear identical. In other words, there is always one unique DC bias current at which both segments develop a finite differential resistance. Figures S1a-c show the differential resistances of two segments of Device S1 as a function of the DC current bias. The black and blue curves represent the I_C^+ (black) and I_C^- (blue) of Segment S1-b, while the red and green curves represent the I_C^+ (red) and I_C^- (green) of Segment S1-c, which is connected and perpendicular to S1-b. Their device geometry is displayed in Main Text Fig. 2a. The zero-field data in Fig. S1a shows no superconducting diode effect (SDE), while a significant SDE emerges at 1 T (Fig. S1b) and -1 T (Fig. S1c).

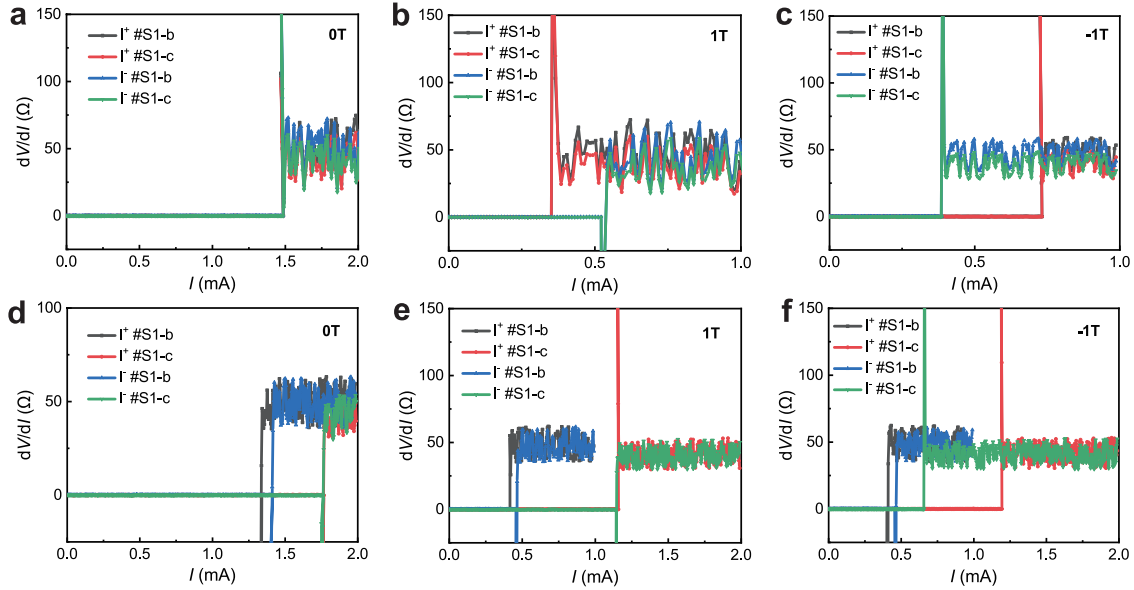


Figure S1: **Measurement of critical currents from connected microstrips.** (a-c) Differential resistances under forward (black for Segment S1-b and red for Segment S1-c) and backward (blue for Segment S1-b and green for Segment S1-c) sweeps of bias current with shared current flow through the entire L-shaped channel at (a) 0 T, (b) 1 T, and (c) -1 T. (d-f) The same as (a-c) except with both segments measured separately.

Given the differing lengths and fabrication details of the two arms, it seems unnatural that they should always have the same critical current under all conditions. Therefore, we separate the measurements to examine individual microstrips in isolation. This doubles the measurement time but yields more plausible results (Fig. S1d-f). When measured separately, they yield different critical currents in both the zero-field (Fig. S1d) and SDE (Fig. S1e-f) cases. Comparing the L-shaped measurement with the isolated measurement, the identical critical currents in the former may be artificially enforced. Despite their intrinsically different critical currents, when one part of the sample undergoes the superconducting-to-normal transition, thermal and electrical fluctuations may disturb the other part of the sample and cause it to prematurely switch to its normal state. Therefore, we adopt the isolated measurement scheme for accuracy.

All data displayed in the main text and all other data in this supporting information are collected via this isolated measurement scheme.

2 Field-odd SDE repeated in a separate sample

The field-odd SDE reported on Device S1 in the main text is reproduced by a second sample. Device S2 is fabricated by first depositing metallic electrodes, followed by reactive ion etching (RIE) to pattern the device into the microstrips geometry. This is a slight variation from the fabrication protocol for Device S1 and Device S3 discussed in the main text, where we etch first and then deposit electrodes. The thickness of Device S2 is measured by AFM to be 15 nm. Fig. S2a shows its optical micrograph and Fig. S2b its resistance-temperature curve typical of β -phased Mo_2C . The residual resistance ratio (RRR) is 1.20, which is the same as Device S-1 and relatively low compared to the α -phase. The sheet resistance of S2 is 43.78Ω at 10 K. Defined at 50% of the normal-state resistance, the superconducting critical temperature T_C of Device S2 is 4.0 K.

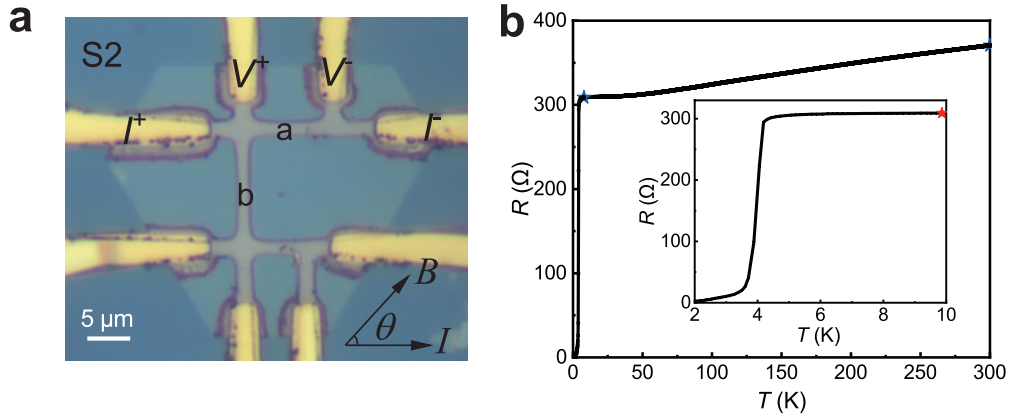


Figure S2: **Sample characterization of Device S2.** (a) Optical micrograph and measurement schematics for Device S2. (b) Electrical resistance as a function of temperature for Device S2. Inset: enlarged view of the superconducting transition region.

For both segments S2-a and S2-b (labeled in Fig. S2a) of Device S2 measured, no obvious superconducting diode effect (SDE) is observed under the in-plane magnetic field parallel to the current flow (Fig. S3a). In contrast, a field-odd SDE appears under the in-plane magnetic field perpendicular to the current flow (Fig. S3b). This behavior is consistent with that observed in Device S1 as reported in the main text.

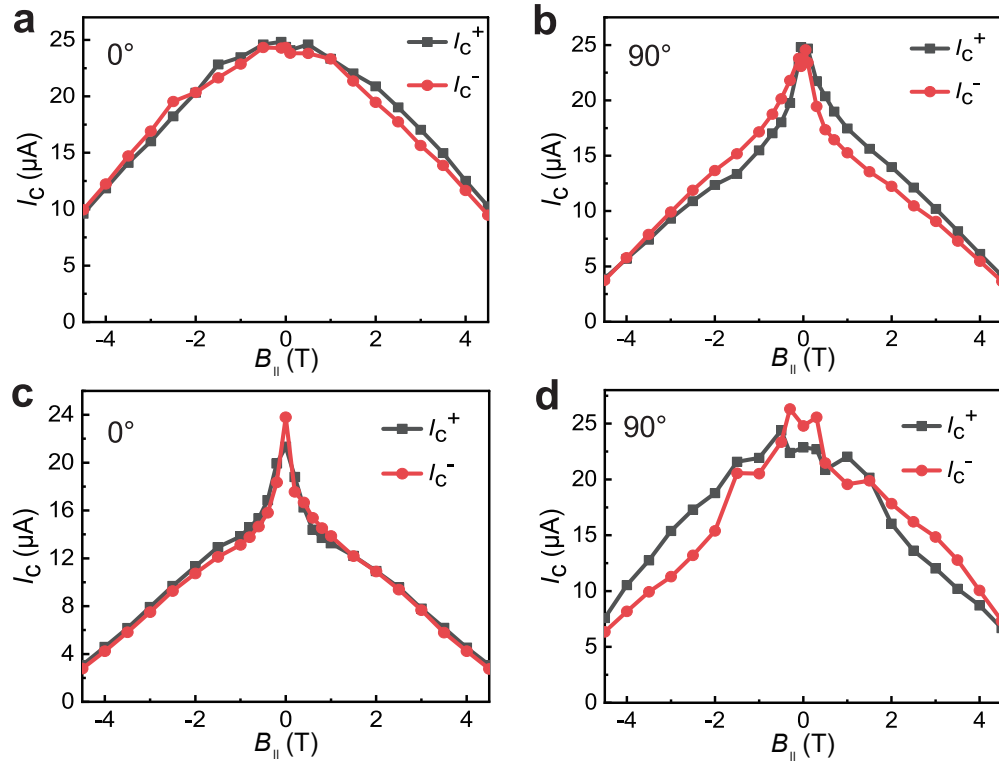


Figure S3: **In-plane field dependence of superconducting critical currents in Device S2.** (a, b) In-plane magnetic field dependence of Segment S2-a's I_C^+ and I_C^- with the field pointing (a) parallel and (b) perpendicular to the current flow direction. (c, d) Same as (a, b) but for Segment S2-b.

3 In-plane magneto-anisotropy and second-harmonic measurement

To verify the symmetry breaking mechanism from Ref. 37 of the main text is at play here, we repeat the measurement of in-plane magneto-anisotropy and second-harmonic resistance. The angle-dependent resistance of Devices S1 and S2 exhibit a prominent two-fold symmetry, indicating that the material's electronic transport properties are governed by a two-fold anisotropy (Fig. S4). This observation suggests the presence of lower crystalline symmetry in the system, consistent with the orthorhombic or distorted electronic order rather than tetragonal, hexagonal, or isotropic symmetries. Because the α -phase is orthorhombic and the β -phase is hexagonal, the interface between them can break spatial inversion symmetry and result in the observed anisotropy.

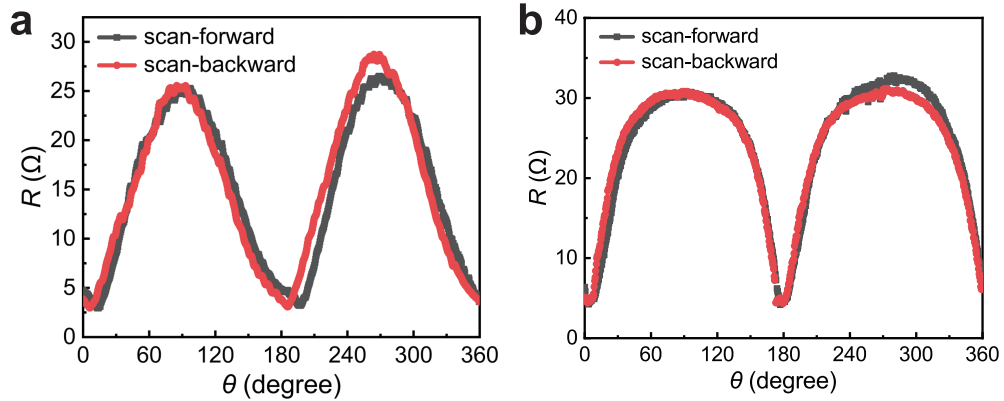


Figure S4: **In-plane anisotropy of Devices S1 and S2.** (a) Angle-dependent resistance of Device S1-a at 6 K and 3 T in-plane magnetic field. (b) Same as (a) but for Device S2-a.

During the field sweep for critical-field characterization, we collect the second-harmonic longitudinal resistance alongside its first-harmonic (Fig. S5). The second-harmonic longitudinal resistance stays zero both in the superconducting state and in the normal state. In the superconducting transition region, it increases in magnitude with increasing magnetic field, showing significant antisymmetric component in positive and negative fields. This behavior reproduces results from Ref. 37 of the main text and makes its reported emerging electronic order relevant to this study because the nonreciprocity observed during the superconducting transition and the SDEs may share similar roots in symmetry breaking.

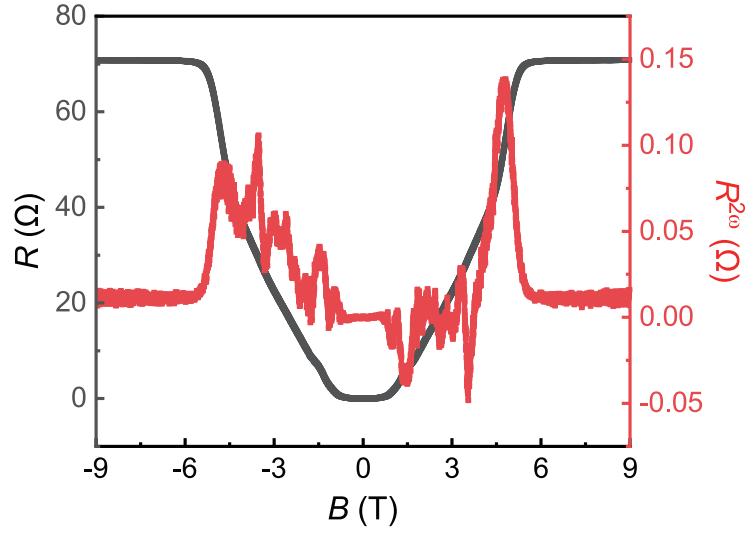


Figure S5: **Asymmetric second-harmonic measurement during superconducting transitions.** First-harmonic and second-harmonic components of the differential resistance versus out-of-plane magnetic field at 1.6 K.

4 Investigating the origin of broken TRS in the field-free SDE

In order to probe whether the broken TRS originates from a magnetic parent phase, we perform hysteresis measurements of Device S3's magnetoresistances. We apply a DC current bias just above its I_C to drive the sample into the normal state. For both segments of Device S3, we sweep the in-plane magnetic field from negative to positive (black curves in Fig. S6) and then back from positive to negative values (red). The resulting DC voltage curves overlap perfectly, indicating no magnetic hysteresis in either segment. This suggests that the field-free diode effect we observe in Device S3 is not caused by any intrinsic ferromagnetism in the parent phase.

By comparing the positive and negative critical currents I_C^+ and I_C^- measured repeatedly from small-range sweeps (only positive or only negative bias ranges without passing zero bias) with those obtained from full-range sweeps between $\pm 300 \mu\text{A}$, we find that the history of current sweeps also does not alter the polarity of the field-free SDE, making a case against the effect originating from accidental vortex pinning (Fig. S7c).

Furthermore, we keep Device S3-b at base temperature 1.6 K and sweep an in-plane magnetic field to ± 1 T. Upon returning to zero field, we find the polarity of the diode polarity unchanged by the coercive field, supporting the intrinsic nature of the device's chirality (Fig. S8).

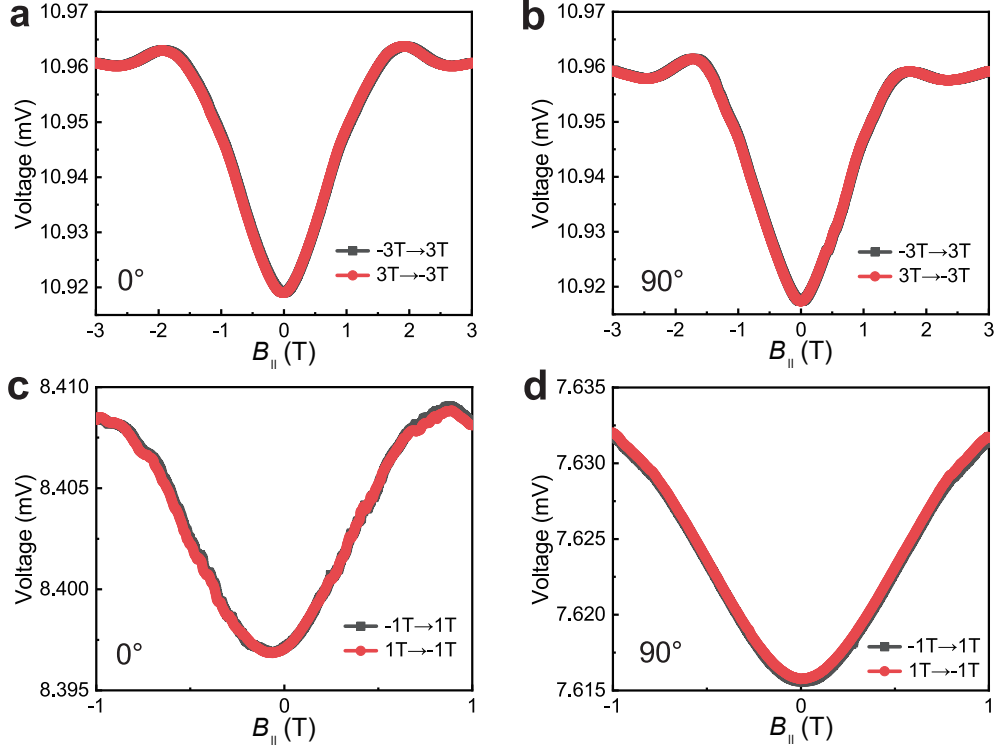


Figure S6: **Absence of magnetoresistance hysteresis in the normal state.** (a, b) DC voltage generated by a current of $300 \mu\text{A}$ as a function of the in-plane magnetic field for Segment S3-a at (a) 0° and (b) 90° angles between the current flow and magnetic field. (c, d) Same as (a, b) but for Segment S3-b.

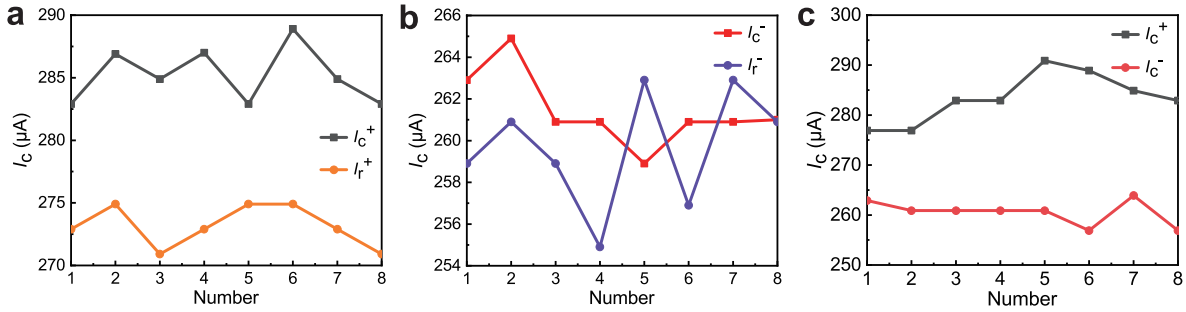


Figure S7: **Superconducting critical currents in Device S3-b.** (a) Repeated measurements of the positive switching current (I_C^+ in black) and positive retrapping current (I_r^+ in orange) while sweeping the bias current between $250 \mu\text{A}$ and $300 \mu\text{A}$. (b) Repeated measurements of the negative switching current (I_C^- in red) and negative retrapping current (I_r^- in purple) while sweeping the bias current between $-250 \mu\text{A}$ and $-300 \mu\text{A}$. (c) Repeated measurements of I_C^+ and I_C^- while sweeping the bias current between $\pm 300 \mu\text{A}$.

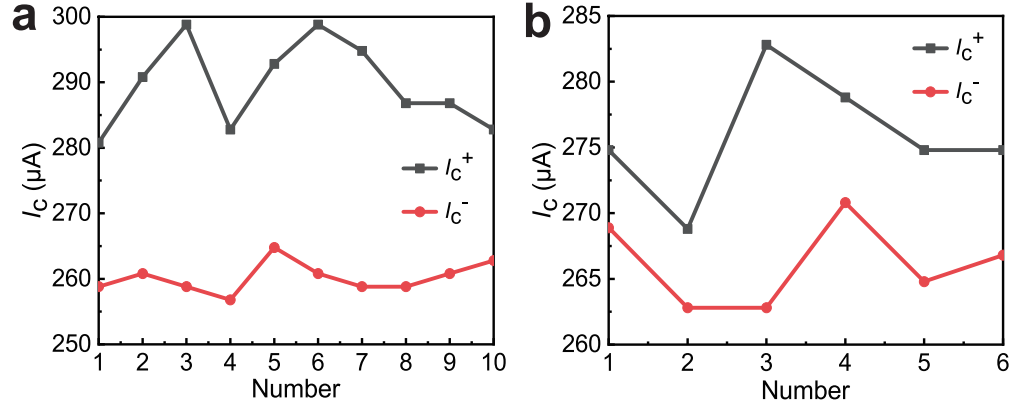


Figure S8: **Unchanging SDE polarity upon low-temperature field sweeps.** Successive readouts of I_C^+ and I_C^- of Device S3-b upon sweeping at 1.6 K an in-plane magnetic field to (a) 1 T and (b) -1 T before returning to zero field.

5 Additional field-free SDE data and investigation of the current-crowding effect

To perform sanity and reproducibility checks, we re-cool Device S3 in our cryostat to acquire additional data. Although Device S3 is a single nanoflake, it contains multiple independent lithographically patterned segments. In Fig. 5 of the manuscript, we present data from two orthogonal microstrip segments, S3-a (Fig. 5c, e) and S3-b (Fig. 5d, f), both of which demonstrate a robust and consistent field-free SDE. Upon this second cool-down, we find the overall critical current drop slightly from the first cool-down, possibly due to minor sample degradation after thermal cycles and storage. The field-free SDE persists for both segments S3-a and S3-b, with the diode polarity unchanged for S3-a and changed for S3-b. This provides new information on the nature of the time-reversal symmetry breaking, which is consistent with the phase-mixing theory, where the coupling parameter between the two superconducting order parameters determine the finite-momentum of the resulting mixed-state superconductivity. The exact direction of the pairing momentum emerges out of a spontaneous rotational symmetry breaking in the Ginzburg-Landau free energy but can be affected by the mesoscopic asymmetries of device geometries, leading it to remain stable at low temperature but can change upon thermal cycling.

In addition to S3-a and S3-b, we have measured a new segment on this sample, S3-c, which wasn't included in the original manuscript. We find its behavior agree with S3-a and S3-b in that it also exhibits field-free SDE which does not reverse polarity upon sweeping the out-of-plane magnetic field (Figure S9). Given the known stochasticity, we again repeat the critical current measurements several times for each configuration.

Current crowding refers to the non-uniform distribution of current density within a conductor, which typically occurs at sharp geometric corners, structural bottlenecks, or interfaces characterized by severe electrical conductivity mismatches. In a mesoscopic superconducting strip, if current crowding becomes sufficiently pronounced, the local current density at a specific edge or corner can reach the critical current density well before the average applied current density across the bulk reaches its nominal threshold. This localized breakdown of superconductivity triggers premature vortex entry or phase slips, leading to an

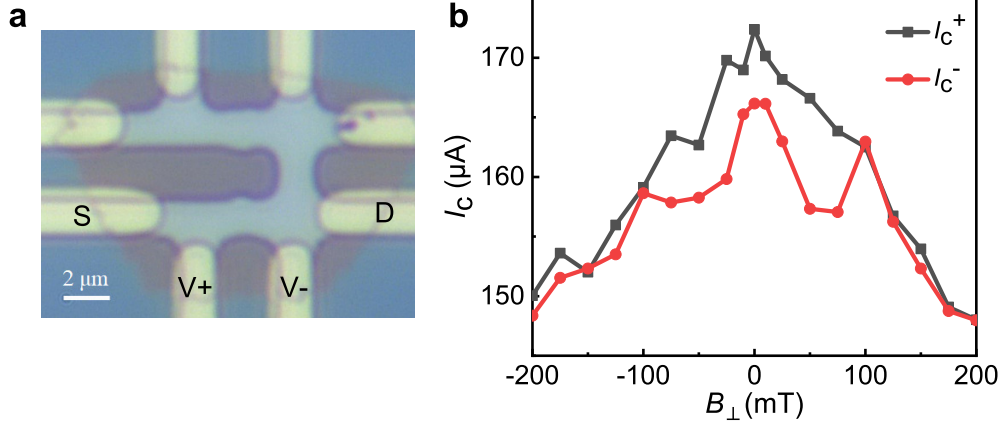


Figure S9: **Measurement in Device S3-c reproduces field-free SDE.** (a) Optical micrograph of Device S3 with measurement configuration for Segment S3-c. (b) Measured critical currents I_C^+ and I_C^- as a function of out-of-plane magnetic field $B_{\perp}$.

early transition to the dissipative state. In our chemical vapor deposition-grown Mo_2C nanoflakes, any slight structural irregularity along the etched edges of the microstrip—such as the visually asymmetric boundaries—or an unintentional misalignment during the lithographic patterning of the voltage probes can skew the current streamlines. This distortion forces the supercurrent to constrict unevenly near one side of the channel.

To definitively rule out extrinsic current-crowding or contact geometry-induced artifacts, we performed control measurements by swapping the source and drain contacts in all three segments of Device S3. We observed no change in the diode polarity or efficiency with respect to the current direction, despite the stochastic noise over repetitions (Figure S10-12). Notice in Figure S10-12, when we swap the source and drain contacts, the same current flow direction goes from I^+ (I^-) to I^- (I^+), so the black (red) line in the upper panel (b) corresponds to the red (black) line in the lower panel (d). This confirms that the observed nonreciprocity is of intrinsic physical origin rather than geometric.

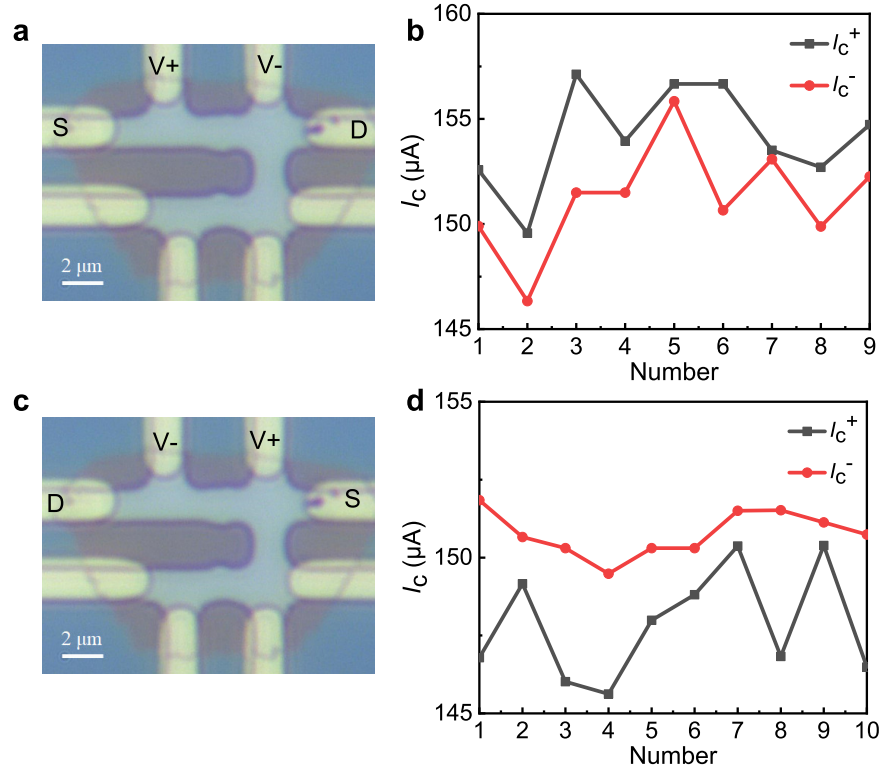


Figure S10: **Ruling out current crowding in Device S3-a.** (a, c) Optical micrograph of Device S3 with measurement configurations for Segment S3-a showing reversed source and drain as well as voltage probes. (b, d) Repeated measured critical currents I_C^+ and I_C^- corresponding to the configuration (a) and (c) respectively.

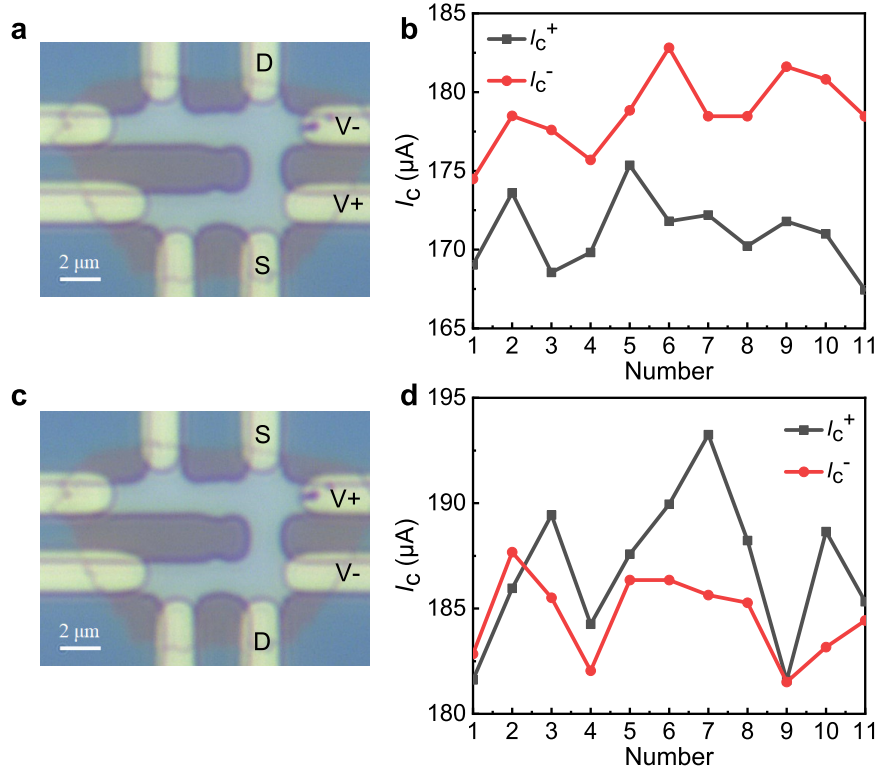


Figure S11: **Ruling out current crowding in Device S3-b.** (a, c) Optical micrograph of Device S3 with measurement configurations for Segment S3-b showing reversed source and drain as well as voltage probes. (b, d) Repeated measured critical currents I_C^+ and I_C^- corresponding to the configuration (a) and (c) respectively.

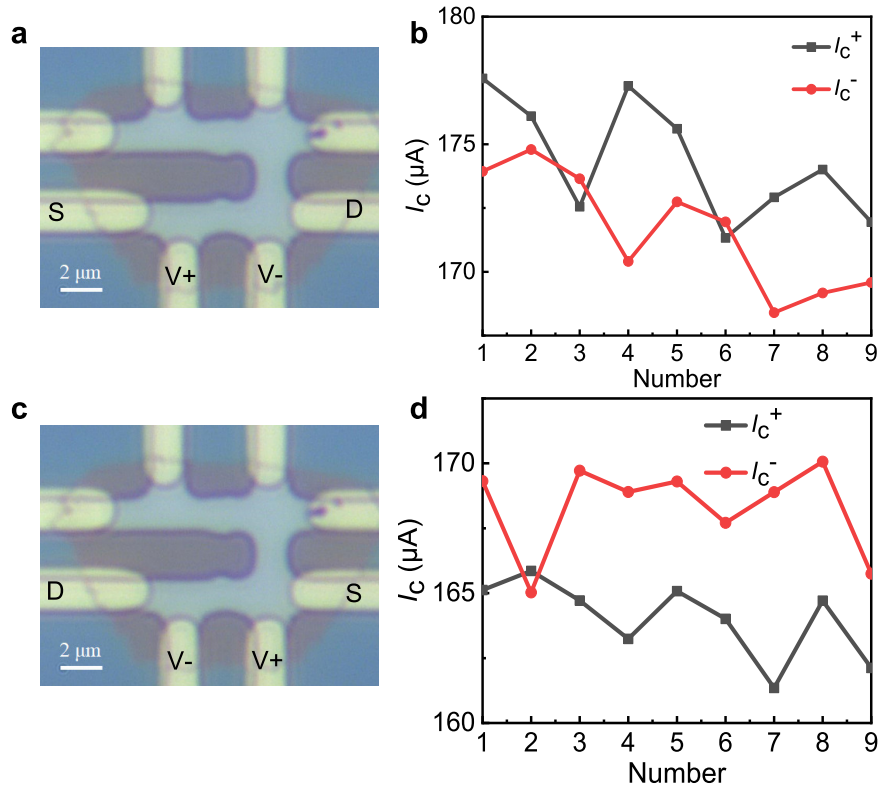


Figure S12: **Ruling out current crowding in Device S3-c.** (a, c) Optical micrograph of Device S3 with measurement configurations for Segment S3-c showing reversed source and drain as well as voltage probes. (b, d) Repeated measured critical currents I_C^+ and I_C^- corresponding to the configuration (a) and (c) respectively.

6 Analysis of the resistance-temperature dependence for possible CDW order

As mentioned in the main text, CDW order is a strong contender for explaining the symmetry breaking in the observed SDEs. Here, we further scrutinize our experimental data, namely the R - T curve, to check for evidence supporting any CDW transitions during the cool down. As demonstrated below, we find a small kink around 96 K for all samples. Since the original R - T data during the cool down is noisy, we perform a smoothing operation on the data to prevent noise-induced fluctuations in the first derivative. Even though this kink is not visible in the R - T curves, a small peak is repeatably evident in the first derivative dR/dT across all three samples at 96, 98, and 95 K respectively (Figure S13), strongly supportive of a phase transition in the phase-mixed Mo₂C which manifests in the electronic transport. This, in combination with the STM data in Ref. 37 and Ref. 39 of the main text, hints at a CDW phase existing in the material below 96 K. However, the fact this kink occurs at the same temperature for samples exhibiting different SDEs suggests this CDW order, if it exists, does not directly determine the SDE physics we observe, at least not single-handedly. That said, again, we cannot rule out CDW as a contributing factor of the SDE given the current evidence.

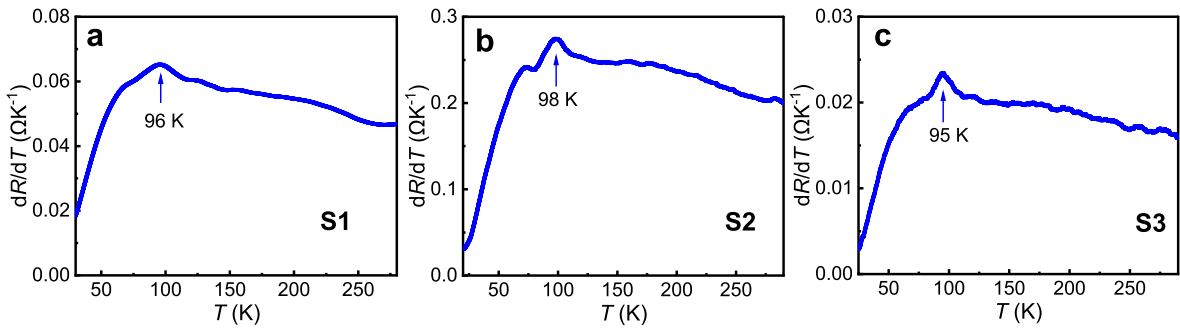


Figure S13: **Derivative of the resistance-temperature relation.** First derivative of the R - T curves for sample S1 (a), S2 (b), and S3 (c) showing a local maximum in dR/dT at respectively 96, 98, and 95 K.