

Dual-Role Ion Dynamics in Ferroionic CuInP2S6: Revealing the Transition from Ferroelectric to Ionic Switching Mechanisms

Corresponding Author: Professor Weiyu Yang

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The 2D ferroelectric materials such as CIPS are interesting, due to their unique "ferroionic" characteristics. This manuscript elucidates the Cu ion migration pathways and their interactions with ferroelectric switching, based on the tip-based SSPFM analyses and first-principles calculations. It is disclosed that the SSPFM and dynamic I-V curves under electric field parameters (bias voltage, time duration, and repeated cycles) match well, providing insights into the conduction mechanism of ferroionic systems. It demonstrates the flexibility to manipulate the migration pathways of Cu ions, achieving a controlled transition from ferroelectric to ion migration-dominated conductive mechanism by varying the electric fields. I recommend it for consideration to be published in Nature Communications after revision. The following points are suggested to the authors for further improving the quality of the manuscript.

1. In Fig. 2, the authors conducted ten consecutive SS-PFM loops at $V_{max}=8V$ to investigate the Cu ion migration-induced abnormal polarization switching behaviors under an electric field. These results are solid evidence of the contribution of Cu ions migration pathways (intralayer or interlayer migration) to the conductive mechanism. Additionally, I suggest the authors conduct the SS-PFM measurement at different V_{max} values.
2. Besides the SS-PFM curves, did the authors conduct PFM imaging measurements to directly observe the ferroelectric domain reversal in response to the electric field applied via the AFM tips? Could the PFM image also reveal the ferroelectric domain reversal oppositely to the electric field direction? The results might be quite interesting and solid evidence.
3. In Fig. 5, by applying a force of 1.4 N, why does the reverse current decrease instead of increasing at high frequencies? This point should be clarified.
4. Page 8, Line 196, "depressed" should be "depress"; Page 8, Line 198, " $E\downarrow P\uparrow$ " should be " $E\uparrow P\downarrow$ ".
5. In the SI information, the figure captions should be more detailed, especially for those not discussed in the main text. Additionally, the caption for Fig. 4 is missing a description for panel 4d.

Reviewer #2

(Remarks to the Author)

In the present work X. Jiang et al. study the van der Waals CuInP2S6 using the PFM techniques and density functional theory calculations. CuInP2S6 and its analogues have gained increased interest in recent years due to possibilities of creating 2D ferroelectric materials for various applications.

The authors describe their switching spectroscopy PFM measurements according to different protocols, which are used to distinguish between ferroelectric switching and the migration of Cu ions in CuInP2S6. Thus, they find ferroelectric switching-dominated and ion migration-dominated regimes of conductivity depending on the applied electric field, which is important for understanding the properties of this and similar compounds.

In principle, I find that the current work could be of interest to the readers of Nat. Commun. if the authors provide sufficient comments on the following issues.

Major concerns:

1. The authors should more clearly state what are the new findings of their work compared to Refs. 22, 23 and 26, which also provide PFM measurements supplemented with DFT calculations and discuss quadruple-well states.
 2. What can the authors say about the leakage current (i.e. current unrelated to ferroelectric switching or ion migration) during their measurements and how it influences the interpretation of PFM measurements? In strongly conducting regimes the current is of the order of ~ 0.1 nA (cf. Fig. 3b), which gives a very large charge passed through the tip during half of the cycle. Simple estimates show that it cannot be accounted for only by ferroelectric switching or ion migration. However, if the electronic conductivity is high, how big is it compared to the ionic one? Can the authors somehow estimate how big is what they call "pronounced accumulation and depletion of Cu ions"?
 3. The authors note the bulge formation after the 10th cycle, which is huge and arguably means significant degradation of the sample, that should influence the properties probed by PFM. What can one say about how fast the bulge forms, e.g. what happens after the 4th cycle when P aligns against E?
- Minor comments.
4. In DFT calculations the $4 \times 4 \times 4$ mesh is only appropriate for cubic or near-cubic crystals with comparable a, b, and c lattice parameters. The lattice parameters a and c in CuInP_2S_6 differ by a factor of ~ 2 , which calls for respective changes in the k-point mesh. What was the number of CIPS layers modelled by DFT?
 5. Inclusion of some van der Waals correction in the DFT calculation scheme should be appropriate and necessary. Furthermore, PBEsol instead of PBE might give more reliable results.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

To well address the relationship between Cu ions dynamics and the conductive mechanisms in CIPS through combining SS-PFM and I-V measurement, distinguishing the contribution of polarization switching, Cu ions migration, and electrons drift to the leakage current is important, as the current work focused. Overall, I think this manuscript is interesting, and the quality of this paper is much improved after revision. After reading the referee comments from reviewer #2, I think one small point can be added to further promote the impact of this work.

1. Objectively, electronic current, ions migration, and polarization switching should occur at different time scales. The time-resolved current measurement on different time scales may be useful to distinguish electronic conductivity and ionic conductivity, which would be also of help to answer the concern of Reviewer #2.

Reviewer #2

(Remarks to the Author)

In the revised version the authors improved the presentation of their findings adding additional studies and sufficient rebuttal of the concerns raised by the reviewer. I think that the work can be published in Nature Communications in the present form.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have answered all the questions. I think this manuscript can be published now.

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Dear reviewers,

We are truly grateful to two reviewers for the valuable comments and suggestions to improve the quality of our manuscript. We have made significant revisions to our manuscript, including additional experiments and detailed analysis. Please see the point-by-point response to the comments below and the revisions in our revised manuscript are highlighted in red color.

Sincerely,

On behalf of all the authors

=====

Responses to Reviewer #1:

Overall Comment: The 2D ferroelectric materials such as CIPS are interesting, due to their unique "ferroionic" characteristics. This manuscript elucidates the Cu ion migration pathways and their interactions with ferroelectric switching, based on the tip-based SSPFM analyses and first-principles calculations. It is disclosed that the SSPFM and dynamic I-V curves under electric field parameters (bias voltage, time duration, and repeated cycles) match well, providing insights into the conduction mechanism of ferroionic systems. It demonstrates the flexibility to manipulate the migration pathways of Cu ions, achieving a controlled transition from ferroelectric to ion migration-dominated conductive mechanism by varying the electric fields. I recommend it for consideration to be published in Nature Communications after revision. The following points are suggested to the authors for further improving the quality of the manuscript.

Response: We appreciate our grateful thanks to reviewer's high recommendation and valuable comments.

Comment 1: In Fig. 2, the authors conducted ten consecutive SS-PFM loops at $V_{\max}=8$ V to investigate the Cu ion migration-induced abnormal polarization switching behaviors under an electric field. These results are solid evidence of the contribution of Cu ions migration pathways (intralayer or interlayer migration) to the conductive mechanism. Additionally, I suggest the authors conduct the SS-PFM measurement at different V_{\max} values.

Response: Many thanks to reviewer's nice and helpful comment. As directed by the reviewer, we have conducted the SS-PFM measurement at different V_{\max} values, as presented below in **Figure R1**. It is

clear that the Cu ion migration and the abnormal polarization switching behaviors are also influenced by tuning the bias window (V_{\max} values). A larger V_{\max} provides sufficient energy for Cu ions to migrate across the vdW gap, where the polarization aligns against the applied electric field.

Figure R1 have been added into the revised Supplementary Materials (**Supplementary Fig. 10**). Accordingly, some discussion has been introduced in the manuscript to make this point clear. (**Line 27-28, Page 8**)

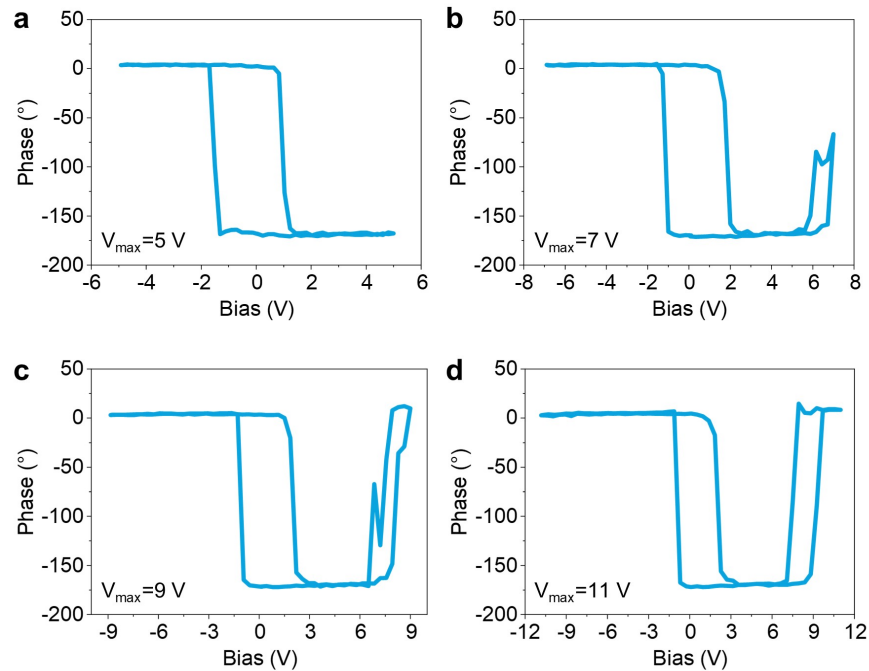


Figure R1. The abnormal switching behaviors modulated by tuning the bias magnitude. a-d The SS-PFM loop measured at different V_{\max} , corresponding to $V_{\max}=5$ V, 7 V, 9 V, and 11 V, respectively. The time duration for each loop is 1 s.

Comment 2: Besides the SS-PFM curves, did the authors conduct PFM imaging measurements to directly observe the ferroelectric domain reversal in response to the electric field applied via the AFM tips? Could the PFM image also reveal the ferroelectric domain reversal oppositely to the electric field direction? The results might be quite interesting and solid evidence.

Response: Many thanks to reviewer’s nice and helpful comment. Actually, we do observe this abnormal behavior, in which the domain reverse against the external electric field. We applied a varying number of pulsed voltages (6 V, 0.5 s) at a single point, with the bias applied through the bottom Au electrode. Then we in situ observe the ferroelectric domains switching process, and the experimental results are shown in below **Figure R2** (The numbers 1-16 represent the numbers of bias pulses at the 4×4 grid point locations). It is evident that in the initial few pulses, the purple ferroelectric domains (downward polarization, \oplus) are switched to yellow ferroelectric domains (upward polarization, \ominus), implying the

ferroelectric polarization aligns with the electric field direction. However, after 13 pulses, the ferroelectric domain switching occurs in the opposite direction to the electric field, as Cu ions start to migrate across the vdW gap interlayer. The surface bulge also rapidly forms due to the Cu ions migrations, and the yellow domains (upward polarization, \odot) begin to switch back to purple domains (downward polarization, \oplus). This result of PFM imaging strongly suggests that the ferroelectric domain reversal oppositely to the electric field direction.

The data in **Figure R2** is our preliminary data. As directed by reviewer, we will perform more detailed and systematic investigation on this topic, which will be reported in a separate work regarding this interesting ferroelectric domain manipulation.

[Figure redacted]

Figure R2. The ferroelectric polarization alignment against the electric field direction, confirmed by the in-situ bias switching and PFM imaging of ferroelectric domain. **a** Different numbers of bias pulses at 4×4 grid point locations. **b-c** The surface morphology and ferroelectric domains changes before and after applying the pulse voltage.

Comment 3: In Fig. 5, by applying a force of 1.4 N, why does the reverse current decrease instead of increasing at high frequencies? This point should be clarified.

Response: Many thanks to reviewer's nice and helpful comment. In the tip force-modulated I-V curves as shown in **Figure R3** (placed in Fig. 5b), the I-V curves are continuously measured at different scanning frequencies (time duration) at 0.7 μN . After that, the tip force is immediately increased to 1.4 μN , and the I-V curves are continuously recorded at the different scanning frequencies (time duration). At 0.7 μN , as the time duration extends, the current significantly increases under positive bias, and

rapidly decreases under negative bias, due to the accumulation and depletion of Cu ions beneath the tip. Such severe depletion of Cu ions leads to lower currents under negative bias at 1.4 μN , as compared to the currents at 0.7 μN over high frequencies (short time duration). Increasing the tip force significantly prevents the rapid current decrease under negative bias, and instead significantly increases the current with the extended time duration. We have introduced some discussion into the revised manuscript to make this point clear. **(Line 21-26, Page 15)**

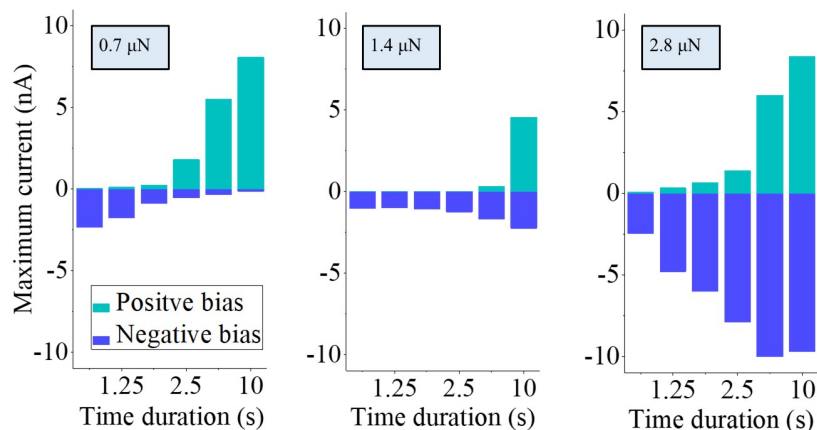


Figure R3. The maximum current (I_{\max}) under two opposite bias directions measured under different tip forces and time durations.

Comment 4: Page 8, Line 196, "depressed" should be "depress"; Page 8, Line 198, " $E\downarrow P\uparrow$ " should be " $E\uparrow P\downarrow$ ".

Response: Many thanks to reviewer's careful review and kind comment. We are sorry to make such errors, which have been corrected in the revised version.

Comment 5: In the SI information, the figure captions should be more detailed, especially for those not discussed in the main text. Additionally, the caption for Fig. 4 is missing a description for panel 4d.

Response: Many thanks to reviewer's careful review and kind comment. We have added more detailed figure caption in SI files, as well as a caption description for panel 4d of Supplementary Fig. 4.

Responses to Reviewer #2:

Overall Comment: In the present work X. Jiang et al. study the van der Waals CuInP₂S₆ using the PFM techniques and density functional theory calculations. CuInP₂S₆ and its analogues have gained increased interest in recent years due to possibilities of creating 2D ferroelectric materials for various applications. The authors describe their switching spectroscopy PFM measurements according to different protocols, which are used to distinguish between ferroelectric switching and the migration of Cu ions in CuInP₂S₆. Thus, they find ferroelectric switching-dominated and ion migration-dominated regimes of conductivity depending on the applied electric field, which is important for understanding the properties of this and similar compounds. In principle, I find that the current work could be of interest to the readers of Nat. Commun. if the authors provide sufficient comments on the following issues.

Response: We appreciate our grateful thanks to reviewer's constructive comments, which help to improve our manuscript a lot. We have addressed all the thoughtful comments as below.

Comment 1: The authors should more clearly state what are the new findings of their work compared to Refs. 22, 23 and 26, which also provide PFM measurements supplemented with DFT calculations and discuss quadruple-well states.

Response: Many thanks to reviewer's nice and helpful comment. Our work is inspired by these outstanding works (Refs. 22, 23 and 26). The major findings that differentiate with Refs. 22, 23, and 26 include: (1) The relation between Cu ion migration dynamics and the conductive mechanisms were not addressed in details in these outstanding studies, which remains unclear. In comparison to Refs. 22, 23, and 26, our work provides solid evidence between the Cu ion migration pathways and the conductive switching behavior; (2) While those references discussed SS-PFM measurements and quadruple-well states, our study further reveals the good agreements between SS-PFM and the I-V curves. Moreover, it is revealed that the intralayer migration leads to ferroelectric-dominated conduction, and interlayer migration contributes to ion migration-controlled conduction, respectively. Furthermore, it confirms that the Cu ion migration pathways in the quadruple state can be manipulated in a deterministic manner depending on the electric fields, achieving a controlled transition from ferroelectric to ion migration-dominated conductive mechanism. These points distinguish our contributions from those works, and we believe the present work could provide some insights into the switching of conductive mechanisms in the CIPS ferroionic system and similar compounds.

As directed by reviewer's advice, we have introduced some discussion into the revised version to make this point clear. **(Line 20-23, Page 3; Line 29-1, Page 3-4; Line 13-21, Page 4)**

Comment 2: What can the authors say about the leakage current (i.e. current unrelated to ferroelectric switching or ion migration) during their measurements and how it influences the interpretation of PFM measurements? In strongly conducting regimes the current is of the order of ~ 0.1 nA (cf. Fig. 3b), which gives a very large charge passed through the tip during half of the cycle. Simple estimates show that it cannot be accounted for only by ferroelectric switching or ion migration. However, if the electronic conductivity is high, how big is it compared to the ionic one? Can the authors somehow estimate how big is what they call “pronounced accumulation and depletion of Cu ions”?

Response: Many thanks to reviewer’s nice and valuable comment. In the SS-PFM measurements, the results include contributions from both ferroelectric capacitance and leakage current. Therefore, as pointed out by reviewer, it should be cautious when interpreting SS-PFM data, especially for the samples with significant leakage current. The CuInP_2S_6 has a wide bandgap of ~ 2.9 eV and exhibits a low leakage current, making it commonly used in gate dielectrics and high-switching-ratio memristors [*Adv. Funct. Mater.*, 34(1): 2306945 (2024); *Nat. Electron.*, 3(8): 466-472(2020)]. In current work, the leakage current is lower than a noise background current of ~ 10 pA at zero bias, implying that the impact of leakage current on the SS-PFM results of this work should be minimal. **Figure R4** further demonstrates the reliability of SS-PFM results. The threshold voltage for the ferroelectric polarization alignment against the electric field in the SS-PFM results is ~ 6 V. Therefore, we apply varying numbers of pulse voltages (6 V, 0.5 s) at different location to observe the ferroelectric domain in response to the electric field. In the initial a few pulses, the purple ferroelectric domains (downward polarization, \oplus) are switched to yellow ferroelectric domains (upward polarization, \odot), suggesting that the ferroelectric polarization aligns with the electric field direction. As the number of pulses increases, particularly after 13 pulses, large area of yellow domains (upward polarization, \odot) begin to switch back to purple domains (downward polarization, \oplus), showing that the ferroelectric domains aligns against the electric field due to Cu ions migration across the vdW gap. The image results of ferroelectric domain switching are highly consistent with that of the SS-PFM switching curve.

[Figure redacted]

Figure R4. The abnormal switching behaviors under an electric field confirmed by SS-PFM and PFM imaging techniques. a The SS-PFM curves measured at different test cycles. **b** The ferroelectric domains switching by applying different numbers of bias pulses at 4×4 grid point locations.

We agree with reviewer that, in strongly conducting regimes, the current can't be accounted solely by ferroelectric switching or ion migration. However, it is very challenging to distinguish the contributions of electronic conductivity and ionic conductivity, due to the strong mutual influence between the two factors. The ion migration also simultaneously has a significant impact on electronic conductivity. The schematic Cu^+ distribution in CIPS under external electric field are shown in below **Figure R5**. During the ion migration, the inhomogeneous distribution of ions inside the material could form an internal electric field along the migration direction, or even a P-N junction [*Mater. Today*, 66: 9-16(2023)., *ACS Nano*, 17(13): 12563-12572(2023), *ACS Nano*, 17(2): 1239-1246(2023)], which significantly influences the electronic transport.

Furthermore, during the migration of Cu ions, the accumulation and depletion of Cu ions at the material interface also influence the Schottky barrier at the electrode-material interface, further impacting the electronic transport [*Nano Lett.*, 21(2): 995-1002 (2021)., *ACS Appl. Electron. Mater.*,

5(10): 5625-5632(2023)]. Conversely, the electronic transport also influences the ion migration. When the electron transport is hindered by the interfacial barrier, the effective voltage applied inside the bulk decreases, making the ion migration more difficult. If we can effectively minimize the impact of ion migration on interfacial contact and avoid the internal electric fields formed inside the material, it may be able to identify the contributions of electronic conductivity and ionic conductivity. This is a very important topic, and we will focus on it in our coming works.

Additionally, when the Cu ions begin to migrate across the vdW gap, the positive current starts to increase sharply, while the negative current begins to decrease sharply. At this point, it is referred to "pronounced accumulation and depletion of Cu ions" under the tip. Thank reviewer once again for this very valuable comment. The revisions have been highlighted in red in the revised version. **(Line 25-2, Page 13-14)**

[Figure redacted]

Figure R5. Schematic Cu⁺ distribution in CIPS under external electric field. **a**, The uniform Cu ions distribution under zero bias. **b-c** The inhomogeneous Cu ions distribution under positive bias and negative bias, respectively. The electric field direction is from "+" to "-" in all cases. [*Mater. Today*, 66: 9-16(2023)]

Comment 3: The authors note the bulge formation after the 10th cycle, which is huge and arguably means significant degradation of the sample, that should influence the properties probed by PFM. What can one say about how fast the bulge forms, e.g. what happens after the 4th cycle when P aligns against E?

Response: Many thanks to reviewer's nice and helpful comment. In the SS-PFM, the pristine surfaces, as well as the surfaces after cycle #7 and cycle #10 are observed, where the significant bulge is formed, as shown in **Figure R6**. As raised by reviewer, we pay attention to what happens when the P just begins to align against E. To better and more convincingly illustrate when the bulge begins to form rapidly, a varying number of pulsed voltages (6 V, 0.5 s) is applied at a single point, with the bias applied through the bottom Au electrode. Accordingly, the surface topography and the ferroelectric domains switching are provided in **Figure R7**. The numbers 1-16 represent the numbers of bias pulses at the 4×4 grid point

locations.

It is evident that, in the initial few pulses, there is no significant bulge formation observed on the surface, where the purple ferroelectric domains (downward polarization, \oplus) are switched to yellow ferroelectric domains (upward polarization, \ominus), implying the ferroelectric polarization aligns with the electric field direction. Interestingly, after 13 pulses, the surface bulge begins to form fast, and large area of yellow domains (upward polarization, \ominus) begin to switch back to purple domains (downward polarization, \oplus), suggesting the ferroelectric domains aligns against the electric field due to Cu ions migration across the vdW gap. Therefore, based on these findings, we conclude that the formation speed of surface bulges does not increase linearly with the bias voltage, but rather exhibits an abrupt change. The intralayer migration of Cu ions seemingly does not cause significant surface changes, while interlayer migration of Cu ions would induce the rapid bulge formation on the surface. Thank reviewer once again for their valuable suggestion to deepen our understanding on this topic.

The data in **Figure R7** is our preliminary data. As directed by reviewer, we will perform more detailed investigation on this topic on the coming days, which will be reported in a separate work regarding this interesting ferroelectric domain manipulation.

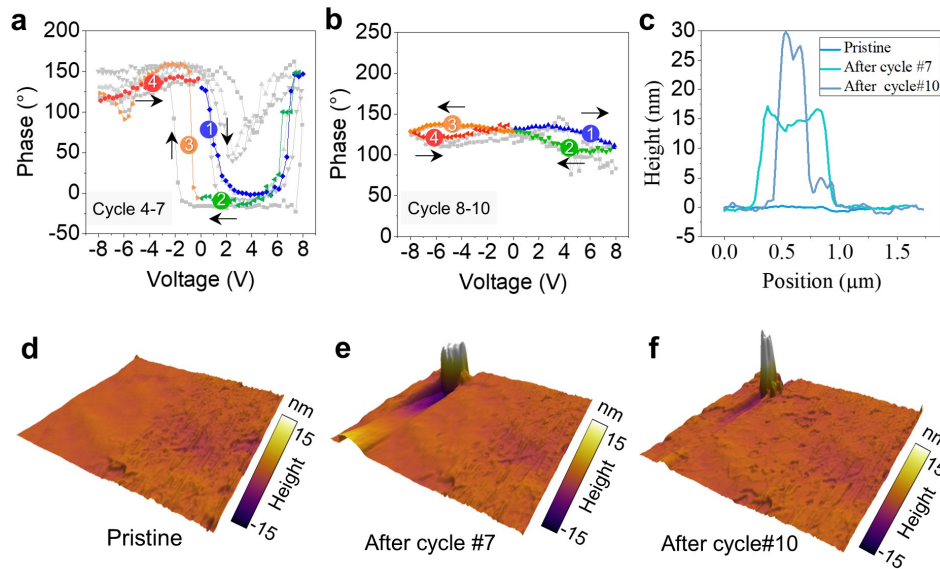


Figure R6. The SS-PFM at different test cycles and the resultant surface bulges. a-b The phase of SS-PFM curves for cycle#4-7 and cycle#8-10, respectively. c The topography of the pristine surface, as well as the heights after cycle #7 and cycle #10. d-f The 3D topography images of the pristine surface and those after cycle #7 and cycle #10.

[Figure redacted]

Figure R7. The ferroelectric domain reversal and surface bulges. **a** Different numbers of bias pulse at 4×4 grid point location. **b-c** The surface morphology and ferroelectric domain switching before and after applying the pulse voltage.

Comment 4: In DFT calculations the 4x4x4 mesh is only appropriate for cubic or near-cubic crystals with comparable a, b, and c lattice parameters. The lattice parameters a and c in CuInP2S6 differ by a factor of ~2, which calls for respective changes in the k-point mesh. What was the number of CIPS layers modelled by DFT?

Response: Many thanks to reviewer's nice and valuable comment. In previous version, the NEB calculation was performed using one unit cell with two CIPS layers. To ensure the uniformity of sampling in *k* space, the *k*-mesh parameter in the Monkhorst-Park scheme is closely related to the lattice parameter. Considering the experimental lattice parameters ($a = 6.096 \text{ \AA}$, $b = 10.565 \text{ \AA}$, $c = 13.187 \text{ \AA}$ and $\beta = 99.12^\circ$) of CIPS, we use 8×4×4 *k*-mesh to re-optimize the unit cell and performed the subsequent NEB calculation in one unit cell, as well as a 2×2×1 *k*-mesh for the NEB calculation in 2×1×2 supercell with four CIPS layers. The migration barrier curve and the atomic structures at the key potential energy points in these two cases are provided in **Figure R8** and **Figure R9**, respectively.

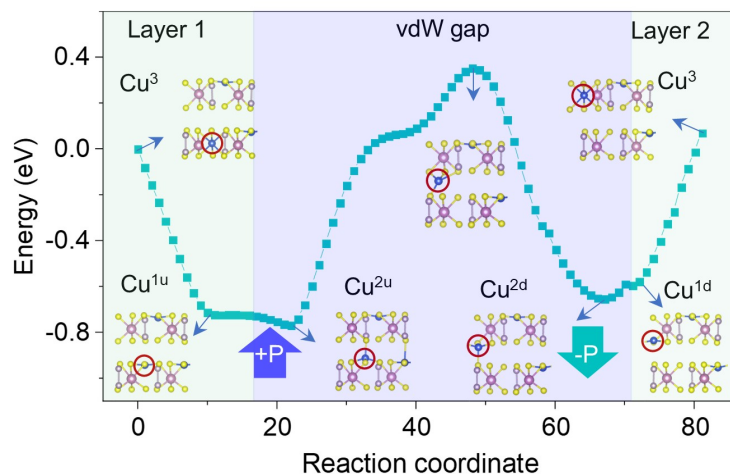


Figure R8. The potential barrier calculated by NEB method for one unit cell with two CIPS layers $8\times 4\times 4$ k -mesh. The atomic structures are placed at the labelled locations of key potential energy points, and the red circles track the migrating Cu ion.

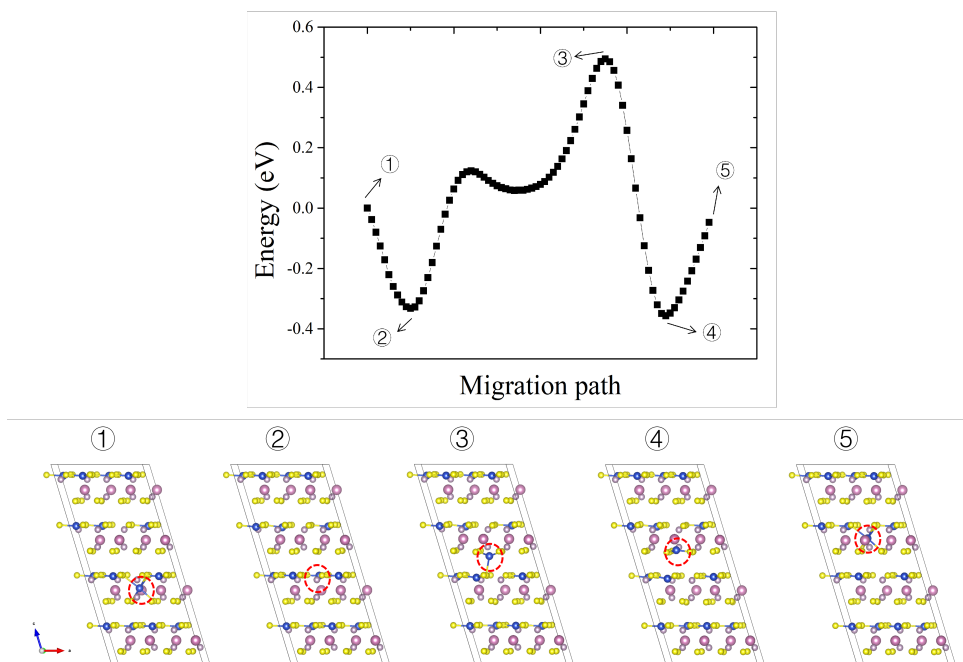


Figure R9. The potential barrier for Cu ion migration across the vdW layer and atomic structure. **Top:** Potential barrier calculated by NEB method for a $2\times 1\times 2$ supercell with four CIPS layers. **Bottom:** The atomic structures at the labelled locations of key potential energy points. The number corresponds to the labelled energy point, and the red circles track the migrating Cu ion.

It can be seen from **Figure R8** that there exists quadruple potential wells when one unit cell with two CIPS layers is used in the NEB calculation. However, when a $2\times 1\times 2$ supercell with four CIPS layers is used in the NEB calculation, there is only double potential wells in **Figure R9**, corresponding to ② and ④ locations, during the Cu ions migration. The system energy changes are further

investigated, where one Cu ion migrates into the gap in a $2\times 1\times 2$ supercell with four CIPS layers. After fixing the lattice constants and other atomic positions, we manually adjust the position of a Cu ion to enter the gap perpendicular to the layer and track the system energy evolution. As shown in **Figure R10**, there exist two potential wells at the labelled potential energy points ① and ②, but their energy difference is relatively small (2.75 meV/f.u.).

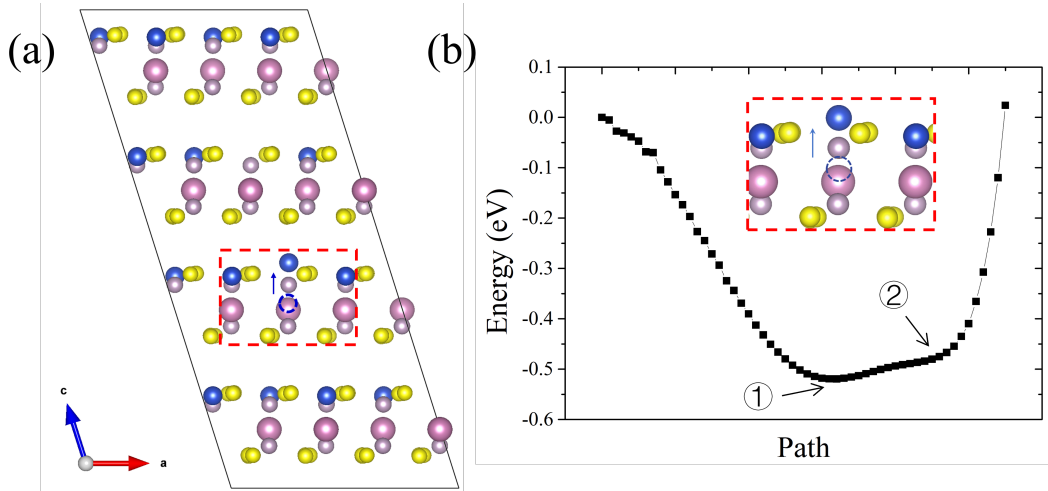


Figure R10. The system energy change during one Cu ion migrates into the gap in a $2\times 1\times 2$ supercell with four CIPS layers. (a) Schematic of one Cu ion moving into the gap, and (b) The corresponding energy change. The red dashed rectangle shows the local structure of Cu ion migration.

When a $2\times 1\times 2$ supercell with four CIPS layers is used in the NEB calculation, which is a case for the low concentration of migratory Cu ion, the simulated migrating Cu ion concentration decreases. Currently, the interaction between the moving ions is weakened, which makes the energy fluctuations of the system smaller. Additionally, the increase in the number of atoms in supercell multiplies the energy of the system, far exceeding the small energy difference between the two local energy minima. Therefore, we think that the simulation of Cu ion crossing by two CIPS layers may be closer to the real experimental situation. In our work, we performed the NEB calculation using one unit cell with two CIPS layers to simulate a Cu ion crossing the CIPS layer gap, which is a case for the relatively high concentration of migratory Cu ion and is also closer to what happens in real experiments. There exists the interactions between Cu ions, which favors the system a more pronounced energy fluctuation.

Thank reviewer once again for this valuable and constructive comment. As directed by reviewer, we have replaced **Figure 2c** in the original version with **Figure R8**. Correspondingly, we have introduced some descriptions in the Methods section. (**Line 17-21, Pages 18; Line 23-25, Pages 18; Line 30-1, Pages 18-19**)

Comment 5: Inclusion of some van der Waals correction in the DFT calculation scheme should be appropriate and necessary. Furthermore, PBEsol instead of PBE might give more reliable results.

Response: Many thanks to reviewer’s nice and valuable comment on computing reliability. As suggested by reviewer, we tested the effects of various electron exchange-correlation functionals (PBE and PBEsol) and vdW corrections (DFT-D2, DFT-D3(0) and DFT-D3(BJ)) on the lattice parameters (a , b , c and β) and lattice volume V , which were also compared with other experimental and theoretical results, as listed in **Table R1**. The results show that the PBEsol function seriously underestimates the lattice parameters (a , b , c). Therefore, after considering both the lattice parameters and lattice volume, we adopted the PBE function to deal with the electron exchange-correlation in the structure optimization of the unit cell and the subsequent NEB calculation. Meanwhile, the DFT-D3(BJ) method was used to correct the vdW interaction. We have added **Table R1** as **Supplementary Table 1**, and replaced **Figure 2c** from the previous version with **Figure R8** in the revised version. Some discussions have been introduced into the revised manuscript to make this point clear. (**Line 17-21, Pages 18; Line 23-25, Pages 18**)

Table R1. Lattice parameters (a , b , c and β) and lattice volume V of bulk CIPS calculated with various exchange-correlation functionals. Experimental and other theoretical lattice parameters at 295 K are also listed for comparison.

Methods	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
PBE+DFT-D2	6.091	10.546	13.788	107.27	845.77
PBE+DFT-D3(0)	6.108	10.580	13.835	107.21	854.05
PBE+DFT-D3(BJ)	6.070	10.512	13.543	107.34	824.35
PBEsol+DFT-D2	5.979	10.341	13.197	107.69	777.36
PBEsol+DFT-D3(0)	6.015	10.415	13.386	107.41	800.22
PBEsol+DFT-D3(BJ)	5.971	10.352	12.974	107.10	766.55
PBE+DFT-D3(BJ) ²	6.068	10.510	13.510	107.34	822.4
Exp. (295 K) ³	6.0956	10.5645	13.6230	107.101	838.5

References

- Zhang, X. *et al.* Origin of versatile polarization state in CuInP₂S₆. *Phy. Rev. B* **108**, L161406 (2023).
- Maisonneuve, V. *et al.* Ferrielectric ordering in lamellar CuInP₂S₆. *Phy. Rev. B* **56**, 10860 (1997).

Dear reviewers,

We would like to thank two reviewers once again for their valuable feedback and insightful comments. In response to Reviewer #1's suggestions, we have conducted the time-resolved current measurement on different time scales. **Please see the point-by-point response to the comments below and the revisions in our revised manuscript are highlighted in red color.**

Sincerely,

On behalf of all the authors

=====

Responses to Reviewer #1:

Overall Comment: To well address the relationship between Cu ions dynamics and the conductive mechanisms in CIPS through combining SS-PFM and I-V measurement, distinguishing the contribution of polarization switching, Cu ions migration, and electrons drift to the leakage current is important, as the current work focused. Overall, I think this manuscript is interesting, and the quality of this paper is much improved after revision. After reading the referee comments from reviewer #2, I think one small point can be added to further promote the impact of this work.

Response: We appreciate our grateful thanks to reviewer's high recommendation and valuable comments.

Comment 1: Objectively, electronic current, ions migration, and polarization switching should occur at different time scales. The time-resolved current measurement on different time scales may be useful to distinguish electronic conductivity and ionic conductivity, which would be also of help to answer the concern of Reviewer #2.

Response: We sincerely appreciate Reviewer's insightful suggestion to consider different time scales as a means to distinguish their contributions, due to much slower ions migration. As directed by the reviewer, we conducted two sets of current measurements at ten consecutive 5 V pulse voltage with pulse widths of 0.01s and 0.1s, as shown in **Figure R1**. The results clearly show that the current for a 0.01s pulse width is much smaller than that for the 0.1s pulse width. The current for a 0.01s pulse width remains relatively stable during 10 consecutive pulses. However, the current for a 0.1s pulse width increases obviously as the number of pulses. In this scenario, ion migration should be dominant. If we attribute the current at these two pulse widths primarily to electronic and ionic conductivity, a simple

estimate suggests that the ionic current is approximately five times greater than the electronic current. However, this topic warrants deeper and more quantitative investigation in our future studies. Once again, we sincerely appreciate the reviewer's valuable suggestions, which have greatly enhanced the quality of this work.

Figure R1 have been added into the revised Supplementary Materials (**Supplementary Fig. 14**). Accordingly, corresponding discussion has been added in the revised manuscript to make this point clear. (**Line 1-4, Page 14**).

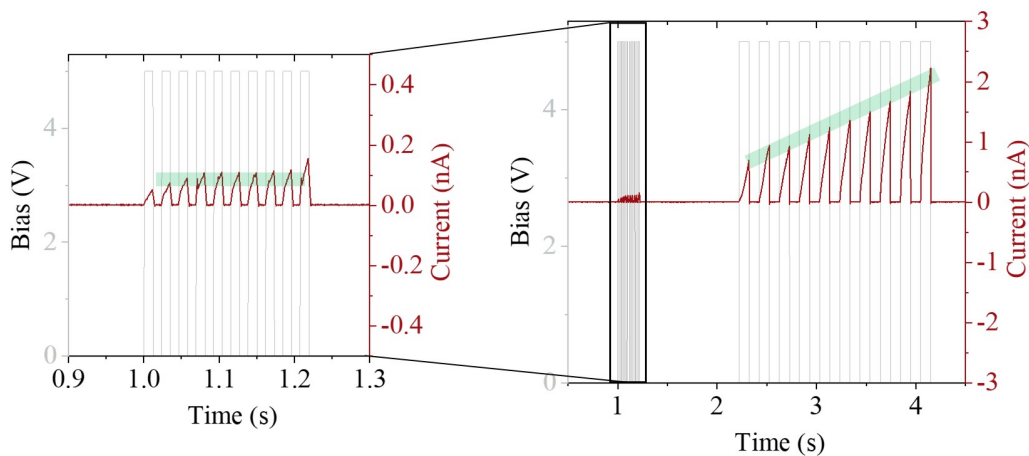


Figure R1. The current in response to two different pulse conditions. The current was measured in response to ten consecutive 5 V pulse cycles with pulse widths of 0.01s and 0.1s, respectively.

Responses to Reviewer #2:

Overall Comment: In the revised version the authors improved the presentation of their findings adding additional studies and sufficient rebuttal of the concerns raised by the reviewer. I think that the work can be published in Nature Communications in the present form.

Response: We appreciate the reviewer for the recommendation for publication in Nature Communications.

Dear reviewers,

We would like to thank two reviewers once again for their recommendation for publication. **Please see the point-by-point response to the comments below.**

Sincerely,

On behalf of all the authors

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Responses to Reviewer #1:

The authors have answered all the questions. I think this manuscript can be published now.

Response: We appreciate our grateful thanks to reviewer's valuable comments and recommendation for publication.