# Electronic Supplementary Information

## Resistive Switching in Benzylammonium-Based Ruddlesden-Popper Layered Hybrid Perovskites for Non-Volatile Memory and Neuromorphic Computing

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## Experimental Section

### Materials

The organic cation salts were purchased from Greatcell Solar, lead compounds were purchased from TCI, and *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were bought from Sigma-Aldrich. All solvents and chemicals were used without further purification.

### Methods

*Mechanosynthesis:* Perovskite powders of $BzA_2PbX_4$ composition (Bz = benzylammonium; X = I, Br) were synthesised by grinding the precursors in the stoichiometric amount in an electric ball mill (Retsch Ball Mill MM-400), employing agate grinding jars with a volume of 5 mL and two stainless steel (5 mm) beads. The grinding time was 30 min at 25 Hz. The materials were loaded into the jars inside a glovebox under a nitrogen atmosphere, and the resulting powders were annealed at 150 °C for 10 min.

*Perovskite thin-film preparation*: Perovskite powders were dissolved in a solvent mixture of DMF and DMSO with a volume ratio of 4:1 (I-based system) or 1:1 (Br-based system) to obtain solutions with a concentration of 0.2 M in accordance with the previous reports.[1–2] The solution-processed films were fabricated using spin-coating. Prior to deposition, the glass substrates were cleaned using sequential ultrasonic treatment with acetone and ethanol for 5 min each, followed by plasma treatment for 5 min. The precursor solution was deposited on the glass substrate and spun at 1000 rpm and 4000 rpm for 10 s and 20 s, respectively. The spin-coated films were then annealed on a hot plate at 150 °C for 10 min. All preparation steps were performed in an argon atmosphere glovebox with oxygen and water levels below 0.5 ppm.

*Device Fabrication:* Before deposition of $(BzA)_2PbX_4$ layers, the fluorine-doped tin oxide (FTO) substrate is cleaned by sonication in acetone, ethanol, and isopropyl alcohol for 14 min each, and subsequently dried under nitrogen gas flow. For spin-coating on the FTO substrate, 0.2 M solutions of $(BzA)_2PbBr_4$ and $(BzA)_2PbI_4$ are prepared by dissolving them in solvent mixtures of DMF and DMSO with volume ratios of 1:1 and 4:1, respectively. Precursor solutions are dispensed onto the FTO substrate and spin-coated at 4000 rpm and 1000 rpm for 20 s and 10 s, respectively. Subsequently, the coated film is subjected to annealing on a hot plate at a temperature of 150 °C for a duration of 10 min. Finally, 100 nm-thick with 500 μm diameter top Al electrodes are deposited by thermal evaporation onto $(BzA)_2PbX_4$ film surface to complete the devices.

*Ultraviolet-visible (UV-vis) absorption spectra* were measured using a Shimadzu UV-2401PC Spectrophotometer at room temperature. *Photoluminescence (PL) measurements* on thin films were performed using a Horiba Fluorolog FL 3-22 (short-arc Xenon discharge lamps as excitation source at 350 nm) spectrometer.

*X-ray diffraction (XRD) measurements* of thin films were performed on a Rigaku Ultima-IV diffractometer using Cu Kα radiation (K-Alpha1 [Å] = 1.54060; K-Alpha2 [Å] = 1.54443) in a Bragg-Brentano configuration. The XRD patterns, complemented with the UV-vis absorption and steady-state PL spectra (Figure S1), evidence the formation of layered (2D) perovskite phases in accordance with the previous reports.[1–3] Unlike previous reports, perovskite materials were prepared by mechanosynthesis followed by solution-processing to form the thin films (Figure S1–S2) that were not further optimised in terms of their morphology or thickness.

*Field emission scanning electron microscopy (FESEM)* measurements were performed on the Apreo 2 Model of Thermo Make.

*The electrical properties* of the device were measured using Keithley 4200 SCS analyzer and 2636B SMU.

## Supplementary Discussion

*The effect of voltage scan frequency:* All devices were recorded using 0.02 V voltage and 8 ms time steps. The sweeps were taken at 6 and 7.5 cycles per minute for Br- and I-based devices, respectively. The execution time in Br- and I-based devices was 10 and 8 s, respectively, for each cycle step remaining constant (0.02 V, 8 ms). The difference in execution time was due to the different voltage range (up to -4 V for bromide and -3 V for iodide system). Otherwise, changing the frequency did not impact the on/off ratio or resistance level (Figure S3).

*The effect of alternative electrodes:* The use of alternative electrodes, such as Ag, affected resistive switching (Figure S4), likely due to the reactivity of the electrode that requires alternative fabrication strategies, such as the use of blocking interlayers in the resulting devices.

*Calculating set and reset voltages:* To calculate the set and reset voltage in the iodide system, the current-voltage characteristics (I–V curve, Figure 2 and Figures S3–S5) were replotted on a linear scale to identify the point where the current starts increasing rapidly, whereas the reset voltage was calculated from the point where the current starts decreasing (Figure S5). For better visibility of the high (HRS) and low (LRS) resistance states, the current-voltage curves were plotted on a logarithmic scale in the main manuscript (Figure 2).

## Supplementary Data

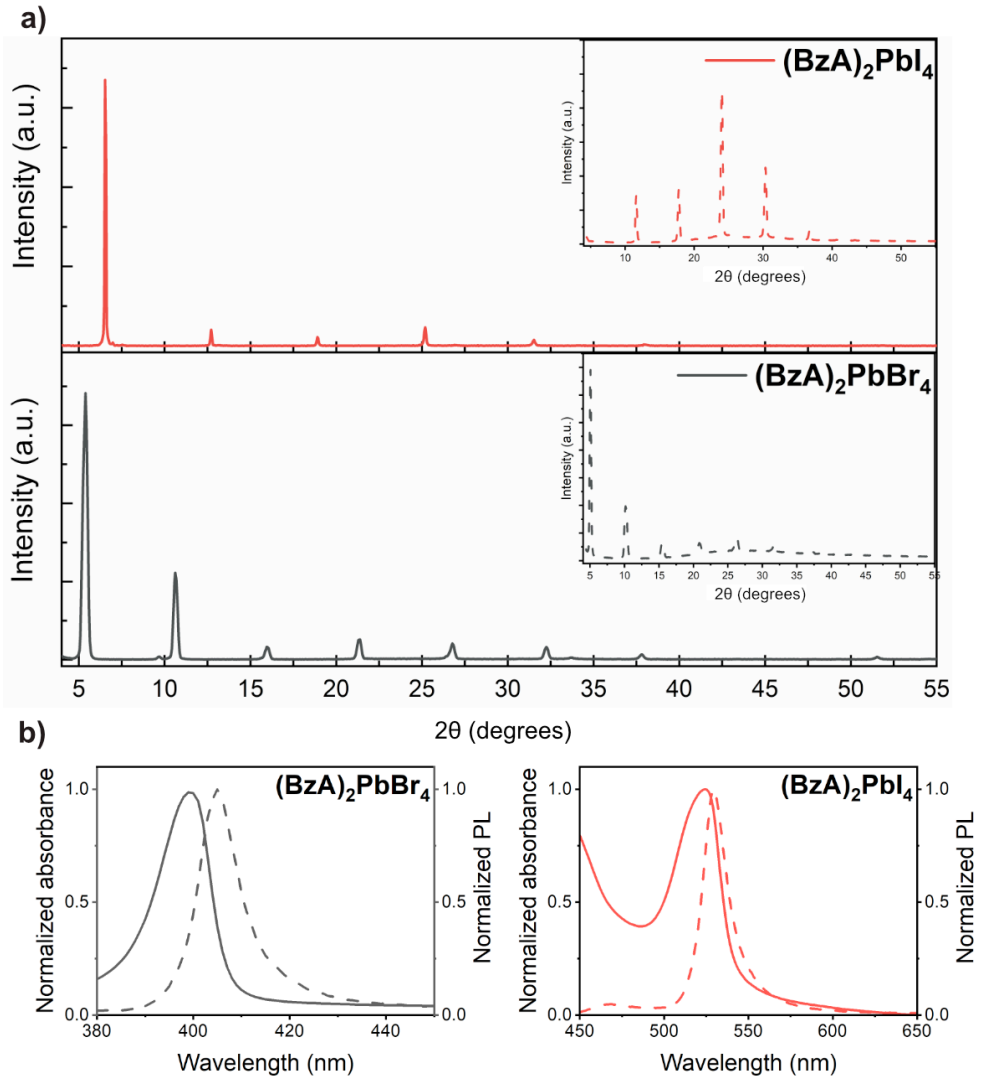


**Figure S1.** (a) X-ray diffraction patterns and the corresponding (b) UV-vis absorption (full line) and PL spectra (dashed line) of $(BzA)_2PbBr_4$ (black line) and $(BzA)_2PbI_4$ (red line) perovskite thin films on FTO (a) and microscope glass (inset of a and b–c), evidencing layered (2D) perovskite formation.[1–3]

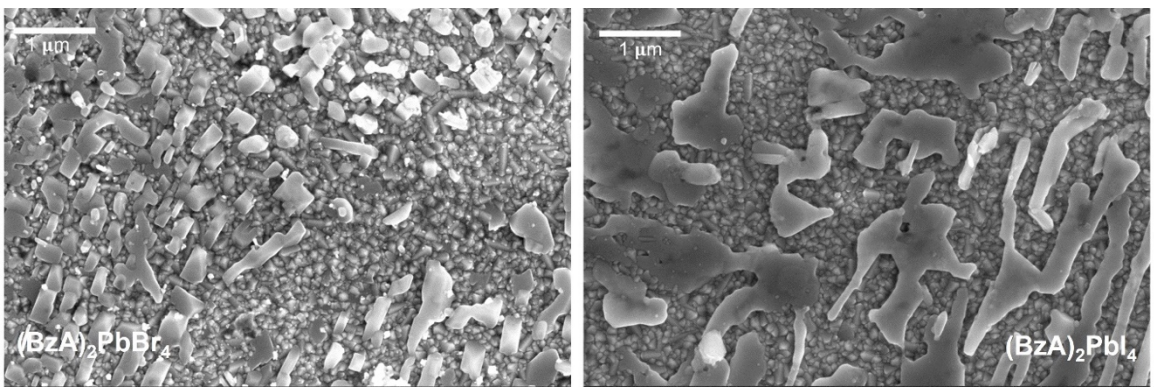


**Figure S2.** SEM images of $(BzA)_2PbBr_4$ (left) and $(BzA)_2PbI_4$ (right) thin films.

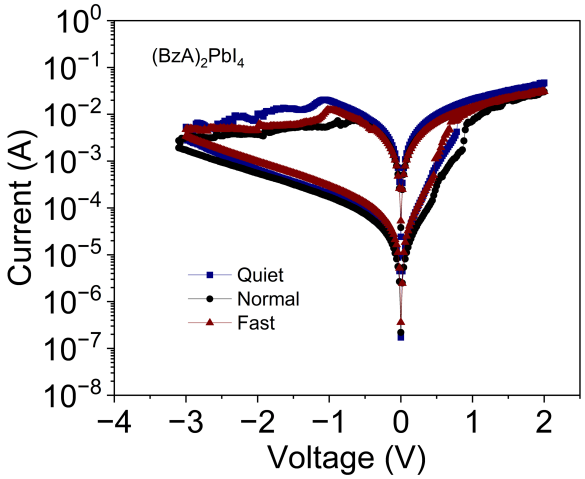


**Figure S3.** Current-voltage characteristics of $(BzA)_2PbI_4$-based device in various time step modes, namely *Quiet* (94 ms), *Normal* (26 ms), and *Fast* (8 ms).

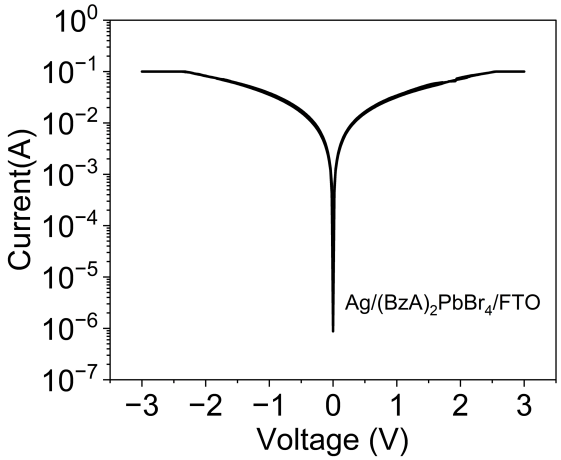


**Figure S4.** Current-voltage characteristic of $Ag/(BzA)_2PbBr_4/FTO$ devices.

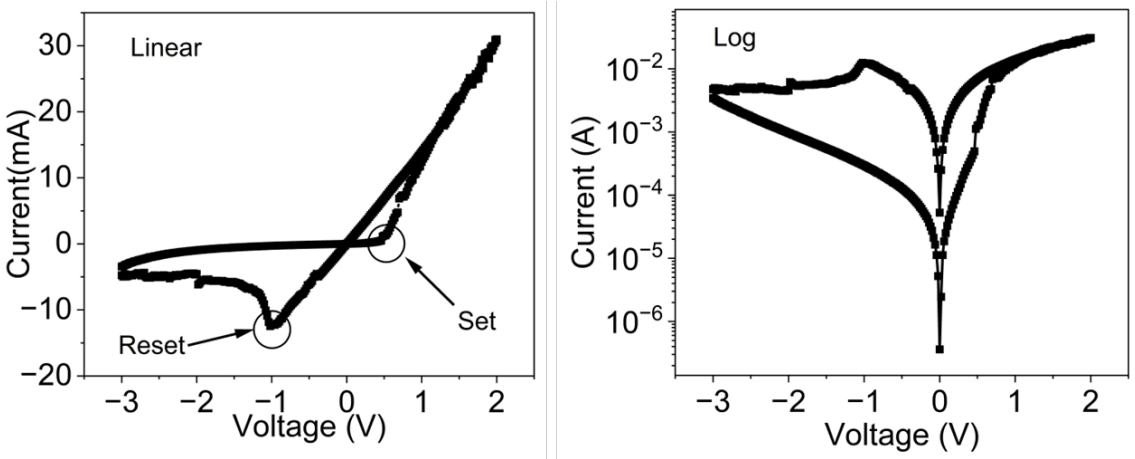


**Figure S5.** Current-voltage characteristics for $(BzA)_2PbX_4$ device on linear (left) and log (right) scale.

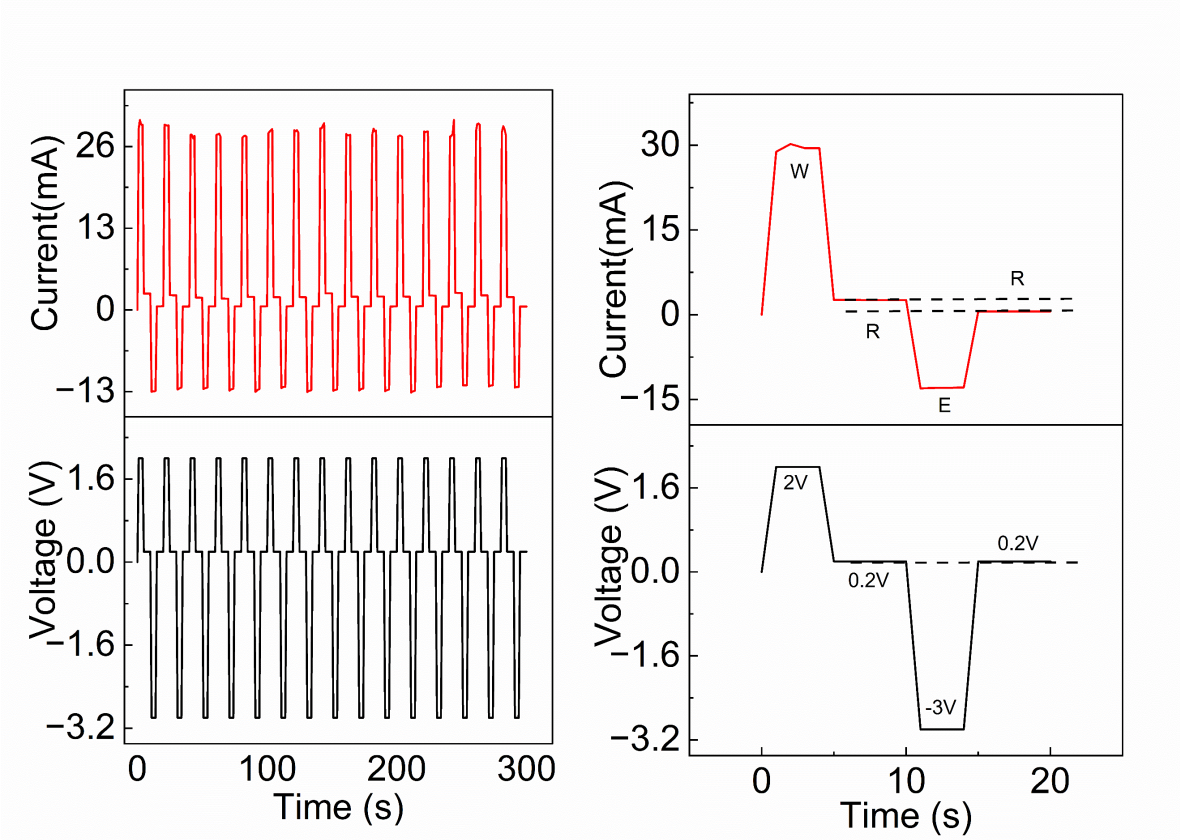


**Figure S6.** Write-Read-Erase-Read cycles for iodide-based perovskite memristor, with enlarged view of 1st cycle on the right.

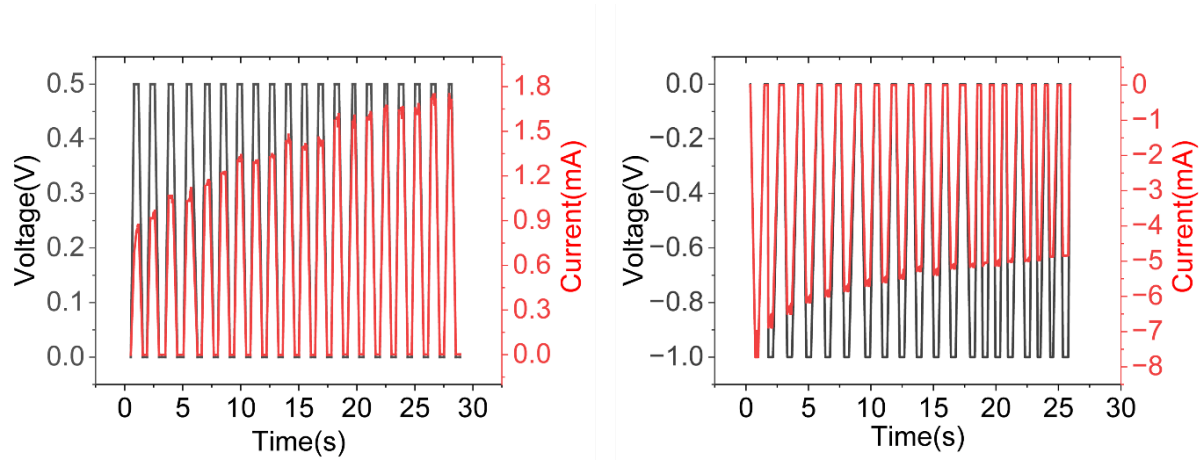


**Figure S7.** Additional scans for potentiation (left) and depression (right) evidencing the reliability of the synaptic behaviour in $(BzA)_2PbI_4$ based devices.

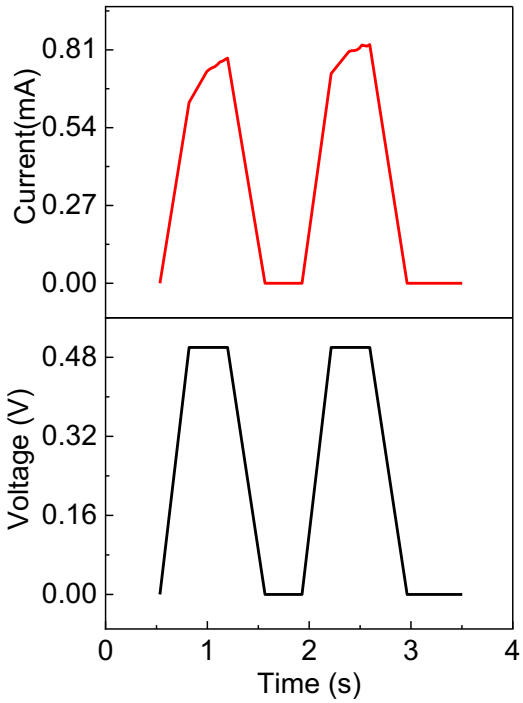


**Figure S8.** Paired-pulse facilitation in iodide-based perovskite system.

## Reference

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