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Supplementary Information

for

Ferroelectricity and Rashba Effect in a Two-Dimensional Dion-Jacobson Hybrid Organic-Inorganic Perovskite

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Methods

Materials characterizations. All chemicals were purchased from commercial vendors (reagent grade) and used as received. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 5 °C/min using a TA Instruments Trios V3.1 thermogravimetric analyzer. Differential scanning calorimetry (DSC) scans were performed under a nitrogen atmosphere with a heating rate of 10 °C/min using Mettler-Toledo DSC. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Focus Powder X-ray diffractometer using Cu K α radiation (40 kV, 40 mA) at room temperature. Solid state diffuse reflectance UV-vis spectra were measured on UV-2450 Shimadzu UV-visible spectrometer equipped with an integrating sphere and barium sulphate as reflecting reference. The solid state fluorescence measurements were made using Horiba Fluorolog using a solid state sample holder (excitation wavelength at 350 nm).

Second harmonic generation (SHG). For SHG measurement, a home-built optical set up was assembled with microscope (Nikon, Eclipse Ti) to measure the SHG of perovskite crystal samples. The laser excitation source with 140 fs pulses, generated by a Ti:sapphire oscillator, has a repetition rate at 80 MHz and a central wavelength at 800 nm. The 800 nm laser beam was cleaned by one 785 nm long pass filter (Semrock, LP02-785RU-25) fixed before the microscope. The perovskite crystals were settled on a 3-D piezo stage (PI P-545). A 10 times objective lens (NA 0.3) focused the beam and collected the SHG signal. The SHG signal of 400 nm was purified by one 750 short pass filter (Semrock, FF01-750/SP-25), following detected by a monochromator (Acton, Spectra Pro 2300i) attached one CCD (Princeton Instruments, Pixis 100B).

Piezoresponse force microscopy (PFM). PFM was performed using a commercial atomic force microscopy (Bruker Dimension FastScan) instrument with conductive PFTUNA probe (Pt/Ir coating, 70 kHz, 0.4 N/m) at ambient atmosphere. In typical PFM measurements, drive frequency and amplitude of 15 kHz and 3000 mV were applied on the tip to acquire out-of-plane PFM image. Local switching spectrum was monitored under a voltage sweep between -8 V to 8 V. The typical scan rate and resolution for all scan modes are 0.5 Hz and 512 pixels. PFM sample was prepared on Au coated Si wafer by spin-coating process and ground to the metallic sample holder with conductive silver paint.

Device measurements. Electrical characterizations were carried out by using Keithley 4200 semiconductor analyzer. The scan direction is -15 V $\rightarrow$ 0 V $\rightarrow$ 15 V $\rightarrow$ 0 V $\rightarrow$ -15 V, with a scan rate of 0.422V/s. The typical current-voltage (I - V) characteristics of the fabricated device were collected following many continuous voltage sweep. The polarization-voltage (P - V) hysteresis loop can be obtained by integrating current over time using following equation:

$$P(V) = \frac{1}{A \times V_{sweep}} \int I dV$$

where the A is area of the capacitor and the V_{sweep} is voltage sweep rate. Furthermore, the capacitance–voltage (C – V) curve can be induced by differentiating polarization over voltage.

Circular polarized photoluminescence (PL) experiments. For circular polarized PL experiments, a 473 nm continuous wave (CW) laser was used to excite the single crystal of **DJP**. The schematic of the experiment is shown in **Figure S11**. The linear polarizer (LP1) was used to clean the initial polarization of the laser (s -polarized). To control the pump circular polarization, a half-waveplate ($\lambda/2$) and a quarter-waveplate ($\lambda/4$) were used. The back-scattered PL was collected and passed through the same $\lambda/4$. Another linear polarizer LP2 was fixed (p -polarized) and placed in the detection beam path. Setting s -polarization as 0° reference, σ^+/σ^- detection can be achieved by setting the $\lambda/4$ fast axis at $+45^\circ/-45^\circ$ (CW/CCW). Meanwhile σ^+/σ^- excitation can be achieved by changing the $\lambda/2$ fast axis to $45^\circ/0^\circ$ when the $\lambda/4$ fast axis is at $+45^\circ$ and to $0^\circ/45^\circ$ when the $\lambda/4$ fast axis is at -45° . By fixing LP2, the signal collected is free from polarization artefacts (e.g., polarization-dependent reflection or grating response). The PL signals from single crystals were detected by a spectrometer (Acton, Spectra Pro 2500i) and charged coupled device (Princeton Instruments, Pixis 400B). An optical cryostat was used to study the circular polarized PL at low temperature. As a control, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ (or PEPI) thin film was measured at room temperature (**Figure S12**). As expected, no circular-polarized emission was observed – hence confirming the accuracy of our setup.

X-Ray Crystallographic Analysis The single crystal X-ray diffraction (SC-XRD) intensity data for **DJP** were measured at room ($T = 298$ K) and high temperature ($T = 373$ K), using a four circle goniometer with Kappa geometry and Bruker AXS D8 Venture Single Crystal X-ray Diffractometer equipped with a Photon 100 CMOS active pixel sensor detector. Data collection, data reduction, and absorption correction were carried out using the software package of APEX3 (Table S1). All calculations for structure determination were carried out using the SHELXTL package.³ Data are available from the corresponding author on request. CCDC- 1939808 (**DJP** at 298K, LTP) and CCDC- 1939809 (**DJP** at 373 K, HTP) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Materials Preparations

Synthesis of 4-(aminomethyl)piperidinium diiodide (AMPI₂). 4-(aminomethyl)piperidine (**AMP**) were purchased from Sigma Aldrich and used as received. **AMP** was used directly to prepare **AMPI₂** by 57% hydroiodic acid (HI).

Preparation of [(AMP)PbI₄], lead(II) iodide 4-(aminomethyl)piperidine Dion-Jacobson perovskite (DJP**).** A mixture of **AMPI₂** (185.0 mg, 0.500 mmol) and PbO (111.6 mg, 0.500 mmol) dissolved in concentrated HI (57 wt.%, 4 mL) was placed in a 20-mL glass vial, followed by the addition of H₃PO₂ (50 wt.%, 0.5 mL). The vial was sealed and kept at 110 °C for 1 hour. Subsequently,

the vial was cooled to room temperature over 30 h. Orange-colored single crystals of **DJP** were obtained.

Device Fabrication. To make the ohmic contact between both sides of **DJP** pellet, the conducting Ag paste was used as an electrode as shown in Figure 5a. First, the Ag paste was painted onto glass substrate to make bottom electrode and put the **DJP** pellet on the Ag paste. The Ag paste was pointed with small area at the surface of **DJP** pellet to make ohmic contact.

Table S1. Crystal data for **DJP** at 298K and 373K

temperature	298K	373K
Formula	C ₁₂ H ₃₂ I ₈ N ₄ Pb ₂	C ₁₂ H ₃₂ I ₈ N ₄ Pb ₂
formula weight	1661.99	1661.99
crystal system	monoclinic	monoclinic
space group	<i>Pc</i>	<i>P2₁/c</i>
<i>a</i> (Å)	10.5315(2)	10.6173(14)
<i>b</i> (Å)	12.5444(3)	12.5400(18)
<i>c</i> (Å)	12.5572(3)	12.530(2)
α (°)	90	90
β (°)	89.985(5)	89.983(6)
γ (°)	90	90
<i>V</i> (Å ³)	1658.95(6)	1668.3(4)
<i>Z</i>	2	2
<i>D</i> _{calc} (g/cm ³)	3.327	3.309
μ (mm ⁻¹)	17.587	17.489
2 θ _{max} (°)	52.00	52.00
reflections collected	19863	15789
independent reflections	5925 [<i>R</i> _{int} =0.0378]	3275 [<i>R</i> _{int} =0.0548]
goodness-of-fit on <i>F</i> ²	1.005	1.024
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0983, 0.2236	0.1234, 0.3313
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0956, 0.2254	0.1327, 0.3423

Figure S1. Photograph of a single crystal of DJP.

Figure S2. PL and absorbance of DJP, showing minimal Stoke's shift, which attests to the quality of the crystal.

Figure S3. Comparison of PXRD patterns for **DJP**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data.

Figure S4. Single crystal structures of **DJP** at (a) 298K and (b) 373K showing Pb(II) coordination environments and asymmetric units. Symmetry operation for A: $-x, 1-y, 1-z$. Since the AMP molecules are situated at the inversion center in (b), they can be inverted and the polarizations are cancelled.

Figure S5. Single crystal structures of **DJP** at (a) 298K and (b) 373K showing packing structures along *c*-axis incorporating $[\text{PbI}_4]^{2-}$ inorganic layers and $[\text{AMP}]^{2+}$ organic layers.

Figure S6. Single crystal structures of **DJP** at (a) 298K and (b) 373K along *b*-axis showing the *Ps* in $[-100]$ equivalent direction.

Figure S7. Single crystal structures of **DJP** at 373K showing (a) the disordered AMP molecules and (b) & (c) 50% occupied AMP molecules. Red-colored balls are inversion centers.

Figure S8. SHG signal of **DJP** collected using a pumping wavelength of 800 nm.

Figure S9. Piezoresponse force microscopy (PFM) for the thin-film of **DJP**. (a) In-plane phase. (c) In-plane amplitude.

Figure S10. The log scale I - V curve of **DJP**.

Figure S11. Schematic diagram for setup for circularly polarized PL measurement for perovskite samples. LP corresponds to the linear polarizers; and BS corresponds to beam splitters.

Figure S12. Circularly polarized PL spectra in thin-film of RP perovskite, (PEA)₂PbI₄ at 293K. Left and right circularly polarized PL under left circularly polarized excitation at 473 nm. No appreciable circular polarized emission was observed.

Figure S13. PL of DJP at 298 K and 373 K. Phase transition from the monoclinic *Pc* (space group No. 3) to the *P2₁/c* (space group No. 14) caused the PL to be blue-shifted and broadened.

Figure S14. Comparison for SHG signals of KDP (potassium dihydrogen phosphate) and **DJP** collected using a pumping wavelength of 800 nm.