Supporting Information

Quasi 3D electronic structures of 2D Dion-Jacobson layered perovskites with exceptional short interlayer distance

Maria Maniadi, Nicolas Mercier,*Alla Skorokhod, Maroua Ben Haj Salah, Pierre Bidaud, Piétrick Hudhomme, Claudio Quarti,* Wei Li, David Beljonne, Jacky Even, Claudine Katan, Constantinos C. Stoumpos

A- Synthesis

A1- Synthesis of 2-iodopropane-1,3-diammonium diodide [(DicI)2+ 2I-



Scheme S1. Synthesis of the (DicI)I2 salt from commercial 1,3- aminopropan-2-ol.

The synthesis of the (DicI)I₂ salt from commercial 1,3- aminopropan-2-ol is described on Scheme S1. To a solution of di-tert-butyl dicarbonate (Boc₂O) (5.2 g, 2.4 eq., 24 mmol) in 60 mL THF was added dropwise a solution of 1,3-aminopropan-2-ol (0.90 g, 1 eq., 10 mmol) in 80 mL of THF / H₂O (1/1, v/v) mixture . The solution was stirred for 24 hours at room temperature. The solvent was partially concentrated under reduced pressure to remove THF and the residue was extracted with diethyl ether. The organic layer was washed with brine, then dried with anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. Recrystallisation in a mixture of diethyl ether and petroleum ether afforded after filtration the white solid -(6.90 g) of di-tert-butyl (2-hydroxypropane-1,3-diyl)dicarbamate in quantitative yield.

To a solution of diamino diprotected molecule (0.725 g, 2.5 mmol) in 10 mL of dichloromethane (HPLC purity) was added distilled triethylamine (0.5 mL, 3.75 mmol). The solution is cooled in an ice bath, then methane sulphonyl chloride (0.23 mL, 3 mmol) is added dropwise. After stirring for 24 hours at room temperature under argon atmosphere, 0.5 mL of water was added and the mesylate compound was extracted with dichloromethane. The organic phase was washed with water, then dried with magnesium sulphate, filtered, and concentrated under reduced pressure. Crystallization using a minimum of dichloromethane and petroleum ether afforded after filtration the mesylate compound (0.76 g) in 83% yield.

The mesylate compound (1g, 2.7 mmol) was introduced into a 10 mL flask and HI acid was added till it covered the compound. The system was plugged by a septum into which a needle was inserted i to create the isobar. The solution was left to stir overnight at 75°C. , Ethyl acetate was then added to the reaction mixture and left for 2 hours in order to completely precipitate the 2-iodopropane-1,3-diammonium diodide [(DicI)²⁺ 2I⁻]salt . The compound was filtered and washed with ethyl acetate. The salt was placed in the oven to dry at 70°C for 1 hour and isolated (1.06 g) in 86% yield.

¹H and ¹³C NMR spectra (Figure S1) were obtained on a 500 MHz Advance III HD spectrometer (500 MHz for ¹H and 125 MHz for ¹³C). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (CD₃OD : $\delta_{\rm H}$ = 3.31 ppm, $\delta_{\rm C}$ = 49.0 ppm).

Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as dd (doublet of doublets), tt (triplet of triplets). Carbon spectra were acquired with a complete decoupling for the proton. ¹H NMR (500 MHz, CD₃OD) *d* (ppm) = 4.42 (tt, *J* = 4.3 and 9.7 Hz, 1H, CH-I), 3.60 (dd, *J* = 4.3 and 14.1Hz, 2H), 3.40 (dd, *J* = 9.7 and 14.1 Hz, 2H).

¹³C NMR (125 MHz, CD₃OD) d (ppm) = 46.0 (CH), 21.3 (CH₂).

MS (MALDI-TOF) : Calcd for $C_3H_{11}I_3N_2$: 455.85; found : 454.62 (M-H)⁺



Fig. S1. a) ¹*H NMR of 2-iodopropane-1,3-diammonium salt in CD₃OD and its enlargment* b) ¹³*C NMR of 2-iodopropane-1,3-diammonium salt in CD₃OD*, c) Mass spectrum (MALDI-TOF) of 2-iodopropane-1,3-diammonium salt

A2- Synthesis of the layered perovskites (DicI)(MA)_{n-1}Pb_nI_{3n+1}

 PbI_2 (99.9%), PbO (99.9%), hydroiodic acid (57 wt % in H₂O, distilled, stabilized, 99.95%), and hypo phosphorous acid solution (50 wt % in H₂O), and MAI (>99.5%) were purchased from Sigma-Aldrich and used as received.

Synthesis of (DicI)PbI₄ (n=1). HI (3mL) and was added to a mixture of PbI₂ (50.0mg, 0.1mmol) and $(\text{DicI})^{2+}$ 2I⁻ (50.0mg, 0.1mmol) in a 20mL scintillation vial, resulting in a mild effervescence (CO₂ emission). The resulting mixture was magnetically stirred to 130°C, resulting in a clear yellow solution. After 30 minutes, stirring was discontinued and the reaction was allowed to cool naturally to ambient temperature. After 30 minutes, red needle-shaped crystals precipitated at the bottom of the vial. The resultant precipitate was isolated via suction filtration and cleaned with ethylene acetate. Yield: 46.8mg (51.09%)

Synthesis of (DicI)(MA)Pb₂I₇ (n=2). HI (5mL) and H₃PO₂ (0.5mL) were added in a 20mL scintillation vial of PbO (334.5mg, 1.5 mmol). After 5 minutes of stirring to 130°C, MAI (159.0mg, 1mmol) was added into the dissolved solution, resulting in a clear yellow solution. In another 20mL scintillation vial $(DicI)^{2+}$ 2I⁻ (114.0mg, 0.25mmol) are dissolved in HI (0.5mL) under heating and stirring to 200°C. After, the vial with the (DicI) becomes a clear solution we add its content into the first vial without any significant change in the color of the solution. The resulting mixture was magnetically stirred resulting in a clear yellow solution. We heat the solution at 200°C until about half of the solvent has evaporated. After 30 minutes, stirring was discontinued and the reaction was allowed to cool naturally to ambient temperature. After 1day, scarlet parallelepiped crystals precipitated at the bottom of the vial. The resultant precipitate was isolated via suction filtration. Yield: 135.8mg (35.35%)

Synthesis of (DicI)(MA)₂Pb₃I₁₀ (n=3). HI (4mL) and H₃PO₂ (0.5mL) were added in a 20mL scintillation vial of PbO (446.0mg, 2mmol). After 5 minutes of stirring to 130°C, MAI (318.0mg, 2mmol) was added into the dissolved solution, resulting in a clear yellow solution. In another 20mL scintillation vial (DicI)²⁺ 2I⁻ (45.6mg, 0.1mmol) are dissolved in HI (0.5mL) under heating and stirring to 200°C. After, the vial with the (DicI) becomes a clear solution we add its content into the first vial without any significant change in the color of the solution. The resulting mixture was magnetically stirred resulting in a clear yellow solution. After 30 minutes, stirring was discontinued and the reaction was allowed to cool naturally to ambient temperature. After 1day, dark-red plate-like crystals precipitated at the bottom of the vial. The resultant precipitate was isolated via suction filtration. Yield: 107.5mg (49.8%)

Crystals of (DicI)(MA)₃Pb₄I₁₃ (n=4). A process similar to that described for the pure phase of $(DicI)(MA)_2Pb_3I_{10}$ (n=3) involving different PbO/MAI ratios, as for instance 3 mmol/2 mmol, leads to a mixture of n= 3 and n= 4 crystals. A selection of a n=4 single crystal allowed solving its crystal structure from SCXRD data.

B- X-ray diffraction characterization

B1- Powder X-ray Diffraction (PXRD)

The Bruker D8 ADVANCE was used to analyze the powder patterns of the synthesized compounds. It is mounted in the Bragg-Brentano geometry in θ -2 θ measurement. The X-rays are formed by a copper anti-cathode of wavelength 1.5406 Å allowing us to obtain a diffractogram of I=f(2θ). The detection angles that measured with this XRD model started from 5° up to 40°. The data collected and analyzed using EVA and OriginPro software, respectively. All experimental XRD patterns seem well fit with the calculated ones obtained from single crystal X-ray data meaning that the n=1, n=2 and n=3 compounds are obtained as pure phases (Figure S2). Comparing the powder patterns for n = 1-3, we observe that all patterns exhibit peaks in different angles. For the n=1, a small characteristic peak shows up right before $2\theta = 10^\circ$, corresponding to the (200) plane, while there is an intense double peak right before $2\theta = 16^\circ$, corresponding to the (020) and (002) planes, respectively. For n=2, some peaks including the first one (right after $2\theta = 5^\circ$, corresponding to (001) crystallographic plane), are not observed in the experimental pattern due to their low signal to noise ratio. An intense peak shows up right after $2\theta = 10^{\circ}$, corresponding to the (002). We also observe an intense double peak right before $2\theta = 15^{\circ}$, corresponding to the (020) and (200) planes. For n=3, we observe a characteristic slightly weak diffraction right before $2\theta = 10^{\circ}$, and an intense peak right above the same angle, corresponding to the (004) and (113) planes, respectively. A characteristic double peak is observed at the PXRD of n=3 as well, right before $2\theta =$ 15° , corresponding to the (020) and (115) planes, respectively.



Fig. S2. Powder X-ray diffraction (PXRD) patterns of the experimental a) n=1 b) n=2 and c) n=3 compounds compared to their calculated patterns.

B2- Single crystal X-ray Diffraction (SCXRD)

X-ray diffraction data were collected on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with Atlas CCD detector and micro-focus Cu-K_{α} radiation ($\lambda = 1.54184$ Å). Data were collected at 293 K. Intensities were corrected for Lorentz-polarization effects, as well as for absorption effect (gaussian method using CrysAlisPro program -CrysAlisPro, Rigaku Oxford Diffraction, V1.171.41.118a, 2021). Crystal structures were solved by charge flipping and refined (full-matrix leastsquares on F²) using the Jana2006 package. CCDC numbers are : 2283257 (n= 1), 2283259 (n= 2), 2283265 (n= 4), 2283266 (n= 3).

	(DicI)PbI ₄	(DicI)(MA)Pb ₂ I ₇	(DicI)(MA) ₂ Pb ₃ I ₁₀	(DicI)(MA) ₃ Pb ₄ I ₁₃			
Crystal System	orthorhombic	orthorhombic	orthorhombic	orthorhombic			
Space Group	C m c e	P b a m	A e a 2	P b a 2			
Unit Cell Dimensions a (Å) b (Å) c(Å) α (deg) β (deg) γ (deg) Volume (Å ³)	a = 20.1168(15) b = 12.6758(10) c = 12.2263(7) $\alpha = 90$ $\beta = 90$ $\gamma = 90$ 3117.7(4)	a = 12.3289(8) b = 12.7636(7) c = 16.2040(9) $\alpha = 90$ $\beta = 90$ $\gamma = 90$ 2793.813	a = 12.3926(5) b = 12.7378(5) c = 44.8986(15) $\alpha = 90$ $\beta = 90$ $\gamma = 90$ 7087.4(5)	a = 12.4176(5) b = 12.7217(5) c = 28.7245(9) $\alpha = 90$ $\beta = 90$ $\gamma = 90$ 4537.7(3)			
Z	8	4	8	4			
Density (gr/ cm ³)	3.9067	4.0032	4.0426	4.0646			
Independent Reflections	1462 [Rint = 0.0916]	2398 [Rint = 0.0789]	6181 [Rint = 0.0732]	8004 [Rint = 0.0784]			
Data/restrains/parameters	1462 / 0 / 66	2398 / 0 / 86	6181 / 9 / 176	8004 / 7 / 212			
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	Robs = 0.0473 wRobs = 0.0519	Robs = 0.0311 wRobs = 0.0329	Robs = 0.0533 wRobs = 0.1129	Robs = 0.0471 wRobs = 0.0966			
R indices [all data]	Rall = 0.0652 wRall = 0.0546	Rall = 0.0451 wRall = 0.0349	Rall = 0.0668 wRall = 0.1180	Rall = 0.0739 wRall = 0.1038			
Fourier Difference max and min (e·Å ⁻³)	5.39 and -1.85	4.77 and -1.24	4.78 and -1.72	2.15 and -2.25			
${}^{a}\mathbf{R} = \sum F_{o} - F_{c} / \sum F_{o} , wR = \{\sum [w(F_{o} ^{2} - F_{c} ^{2})^{2}] / \sum [w(F^{\circ} ^{4})^{1/2} and w = 1/(\sigma^{2}(I) + 0.0004I^{2}).$							

Table S1. Crystal Data and Structure Refinement for $(DicI)(MA)_{n-1}Pb_nI_{3n+1}$



Fig. S3. -a- Part of the structures of $(DicI)(MA)_{n-1}Pb_nI_{3n+1}$ (n=1 to 4, from left to right) showing ADPs ; -b- Definition of axial and equatorial Pb–I–Pb angles in the crystal structures of $(DicI)(MA)_{n-1}Pb_nI_{3n+1}$

(Dicl	[) PbI 4	(DicI)(MA)Pb ₂ I ₇	(DicI)(MA) ₂ I	Pb3I10	(DicI)(MA)a	3Pb4I13
Label	Distances (Å)	Label	Distances (Å)	Label	Distances (Å)	Label	Distances (Å)
Pb(1)-I(1)	3 2250(7)	Pb(1)-I(1)	3 0696(8)	Pb(1)- I(1)	3 182(2)	Ph(1)-I(1)	3 187(5)
Ph(1)-I(2)	3 1529(11)	Ph(1)-I(2)	3 2310(6)	Ph(1)-I(5)	3.039(4)	Ph(1)-I(1)	3 174(5)
$D_{\rm D}(1) (2)$	2 1726(19)	Db(1) I(2)	2 1002(8)	Pb(1) I(7)	2 227(4)	Pb(1) I(2)	3.174(3)
FD(1)-1(3)	3.1730(18)	FD(1)-1(3)	3.1902(8)	FD(1)-I(7)	3.337(4)	PD(1)- $I(2)$	3.1340(17)
		PD(1)-I(4)	3.1897(6)	PD(1)-1(13)	3.242(2)	PD(1)-I(6)	3.1749(17)
		Pb(1)-I(5)	3.2733(5)	Pb(1)-I(8)	3.174(4)	Pb(1)-I(10)	3.2329(5)
				Pb(1)-I(8)	3.196(4)	Pb(1)-I(11)	3.1369(10)
				Pb(2)- I(3)	3.154(3)	Pb(2)-I(4)	3.2432(18)
				Pb(2)-I(4)	3.200(5)	Pb(2)-I(5)	3.189(4)
				Pb(2)-I(7)	3.150(5)	Pb(2)-I(5)	3.172(4)
				Pb(2)-I(10)	3.1764(13)	Pb(2)-I(7)	3.1860(18)
				Pb(2)-I(10)	3.1929(13)	Pb(2)-I(9)	3.0419(13)
				Pb(2)-I(12)	3.177(3)	Pb(2)-I(11)	3.3297(10)
				Pb(3)- I(2)	3.243(3)	Pb(3)-I(13)	3.1801(18)
				Pb(3)-I(4)	3.269(4)	Pb(3)-I(14)	3.2523(18)
				Pb(3)-I(6)	3.069(4)	Pb(3)-I(18)	3.188(4)
				Pb(3)-I(11)	3.187(4)	Pb(3)-I(18)	3.174(4)
				Pb(3)-I(11)	3.182(2)	I(3)-Pb(3)	3.3045(10)
				Pb(3)-I(14)	3.184(2)	I(8)-Pb(3)	3.0513(13)
						I(3)-Pb(4)	3.1463(10)
						I(10)-Pb(4)	3.1837(5)
						Pb(4)-I(15)	3.1578(17)
						Pb(4)-I(16)	3.1654(17)
						Pb(4)-I(17)	3.179(6)
						Pb(4)-I(17)	3.182(6)
Average	3.1838		3.1908		3.1863		3.1827

Table S2. Selected bond distances for $(DicI)(MA)_{n-1}Pb_nI_{3n+1}$

	(DicI)PbI4	(DicI)(MA))Pb ₂ I ₇	(DicI)(MA)2Pt	03I 10	(DicI)(M	IA)3Pb4I13
Label	Angle (°) Axial	Label	Angle (°) Axial	Label	Angle (°) Axial	Label	Angle (°) Axial
		Pb(1)-I(5)- Pb(1)	158.20(10)	Pb(1)-I(7)-Pb(2)	158.49	Pb(2)-I(11)-Pb(1)	158.78
				Pb(2)-I(4)-Pb(3)	158.93	Pb(1)-I(10)-Pb(4)	160.28
						Pb(4)-I(3)-Pb(3)	159.17
Average			158.20(10)		158.71		159.41
	Angle (°)		Angle (°)		Angle (°)		Angle (°)
Label	Equatorial	Label	Equatorial	Label	Equatorial	Label	Equatorial
Pb(1)-I(3)-Pb(1)	180	Pb(1)-I(3)-Pb(1)	178.74(25)	Pb(2)-I(10)-Pb(2)	178.73	Pb(1)-I(1)-Pb(1)	179.78
Pb(1)-I(1)-Pb(1)	143.47(7)	Pb(1)-I(4)-Pb(1)	149.75(10)	Pb(3)-I(11)-Pb(3)	179.63	Pb(4)-I(17)-Pb(4)	178.73
		Pb(1)-I(2)-Pb(1)	146.50(10)	Pb(1)-I(8)-Pb(1)	178.48	Pb(3)-I(18)-Pb(3)	179.49
				Pb(3)-I(2)-Pb(3)	148.36	Pb(2)-I(5)-Pb(2)	178.69
				Pb(2)-I(3)-Pb(2)	157.61	Pb(1)-I(2)-Pb(1)	158.71
				Pb(2)-I(12)-Pb(2)	155.29	Pb(2)-I(4)-Pb(2)	149.16
				Pb(1)-I(3)-Pb(1)	148.95	Pb(4)-I(5)-Pb(4)	160.48
				Pb(1)-I(1)-Pb(1)	150.61	Pb(4)-I(16)-Pb(4)	156.12
				Pb(3)-I(14)-Pb(3)	150.75	Pb(2)-I(7)-Pb(2)	151.36
						Pb(3)-I(13)-Pb(3)	150.44
						Pb(3)-I(14)-Pb(3)	149.48
						Pb(1)-I(6)-Pb(1)	156.69
Average	161.47		158.33		160.93		162.43

Table S3. Selected bond angles for the $(DicI)(MA)_{n-1}Pb_nI_{3n+1}$ compounds

C- Thermal and optical characterization

C1- Thermal characterization

Thermogravimetric analysis (TGA). A full set of data were adopted via Diamond TGA set up, which was purchased from Perkin Elmer Company. The TGA device consists of an electronic high accuracy weight scale, which is connected with a high temperature oven surrounding the supplement area. Data were measured in the 25-600 °C (n= 2), 25-800 °C (n= 1), 25-1000 °C (n= 2), under a continuous N₂ flow at a flow rate of 200 mL/min.

The thermogravimetric analysis curves are provided Figure S4. All the thermal diagrams exhibit very similar trends in the temperature regions of ~200°C and ~400°C. The thermal decomposition starts at ~200 °C, with the evaporation of the organic part. For n=1 (53.59%), this corresponds to ~1 (DicI) and 2HI, per formula unit and for n=2 (37.41%) and n=3 (31.53%), it corresponds to ~1(DicI) 3HI and MAI. At temperatures around 400°C, all diagrams display a significant mass loss of PbI₂. For n=1 (52.27%) this corresponds to ~1 PbI₂, per formula unit, while for n=2 (51.44%) and n=3 (60.01%), that corresponds to ~2 PbI₂ and ~3 PbI₂ per formula unit, respectively.

Differential Scanning Calorimetry (DSC). A full set of data were collected via DSC-250 for all n=1-3 compounds. Approximately 2.3 mg of each sample were placed in aluminum pans which were then hermetically closed. They were placed in the calorimeter along with an empty reference pan. The samples were first maintained in a 2 min isothermal state and then heated from 30 °C up to 170 °C with a rate of 10 °C/*min*. The samples then maintained in a 2 min isothermal state and then cooled from 170 °C down to 30 °C with a rate of 10 °C/*min*. The process was repeated twice, with the first cycle discarded as it was performed only to erase the samples thermal history.

The DSC diagrams for the 3 compounds are provided Figure S4. No endothermic nor exothermic peaks were observed in the 30°C-170°C range meaning in particular that no phase transition takes place in the studied temperature range.



Fig. S4. Thermogravimetric analysis (TGA) (a-c) and Differential Scanning Calorimetry (DSC) diagrams (d-f) of the n=1, 2 and 3 compounds.

C2- Optical characterization

Optical Absorption Spectroscopy. Optical diffuse reflectance measurements were performed using a Shimadzu UV-2600 plus UV-vis-NIR spectrometer operating in the 185-1400 nm region using BaSO₄ as the reference of 100% reflectance. The optical band gap of the material was estimated by converting reflectance to absorption according to the Kubelka-Munk equation: $\frac{\alpha}{s} = \frac{(1-R)2}{2R}$, where R is the reflectance and α and S are the absorption and scattering coefficients¹ respectively.



Fig. S5. Fitting of the absorption spectra leading to the optical values of 2.12 eV ((DicI)PbI₄ - n=1-), 1.98 eV ((DicI)(MA)Pb₂I₇ - n=2-), 1.76 eV ((DicI)(MA)₂Pb₃I₁₀ - n=3-), and 1.53 eV (MAPbI₃).

Photoluminescence Spectroscopy (PL). Photoluminescence spectra were collected on oriented crystals of the $(Dic)(MA)_{n-1}Pb_nI_{3n+1}$ perovskites (n = 1-3) using Horiba LabRam Evolution high resolution confocal Raman microscope spectrometer (600 g/mm diffraction grating) equipped with a diode CW laser (532 nm, 35 mW) and a Synapse CCD camera. The incident laser beam was parallel to the (010) direction of the crystals and focused at ~1 µm spot size. Unless stated otherwise, the maximum power output of the laser source was filtered to 0.01% of the maximum power output.

D- Theoretical analyses and simulations

Lattice mismatch analysis. In the framework of the lattice mismatch model for multilayered 2D perovskites⁵, the possible accumulation of strain within the perovskite lattice for intermediate n values is evaluated from the relative difference between the in-plane lattice parameters of the n=1 compound of the series and the lattice parameter of the 3D perovskite reference (here MAPbI₃). The evolution of the in-plane lattice parameter as a function of n, is characteristic of the strain relaxation in the lattice. Very large mismatches prevent systems from forming materials with high n values, as the accumulation of strain energy scales as the square of the lattice mismatch⁵. This situation is encountered in the PEA series, which exhibits a larger (negative) mismatch than the BA series (Figure S6). We may notice that the DJ 3AMP series presents a positive mismatch on the same order as the one of the BA series, leading also to the observation of multilayered compounds up to n=4. The new Dicl-based DJ series reported in the present work is in a favorable situation, with a limited negative lattice mismatch, explaining the possible formation of multilayered compounds up to n=4.



Fig. S6. Lattice mismatch analysis in multilayered 2D perovskites⁵. The evolution of the experimental room temperature in-plane average lattice parameter of classical RP (green dotted lines for BA and PEA series⁶) and DJ (blue continuous line for the 3AMP series²) multilayered perovskites. The blue dotted line is reported for the new Dicl series of the present work. The red area represents the typical lattice parameter range found experimentally for the reference 3D perovskite MAPbI₃^{7,8}.

Band structure calculations. Periodic DFT calculations have been performed within the planewave/pseudopotential formalism, as implemented in the Quantum-Espresso suite^{9, 10}. As reported in the main text, these are based on standard GGA method for the description of the exchange and correlation potential, as proposed by Perdue *et al.*,¹¹ and performed within the non-collinear spin description, with inclusion of spin-orbit-coupling. Energy cutoff for the planewave expansion of the single particle states and electronic density was set to 25 Ry and 200 Ry, respectively, along with ultrasoft pseudopotentials¹². The present computational set-up was shown to provide good trade-off between accuracy and computational cost¹³. Periodic models from single-crystal XRD were used as reference for calculations. Van der Waals interactions were included using the DFT-D2 method¹⁴, for the optimization of the atomic positions of the organic component. Due to similar in-plane lattice parameters for the various, we used same 3x3 automatic sampling of the Brillouin zone¹⁵, for the reciprocal directions associated to the inorganic plane. Out of plane sampling instead reflected the length of the direct lattice parameter associated with the plane-stacking (final samplings corresponding to 3x3x2, for n=1,2,4 and n=3x3x1 for n=3).

Dielectric profile calculations. Dielectric profiles were calculated following the procedure in Ref. ¹⁶. It consists in performing electronic structure calculations of periodic slabs of 2D halide perovskites and evaluating the variation of the electronic density following application of electric field (0.01 V/Å) along the plane stacking direction. Periodic DFT calculations are performed using atomic-centered, periodic DFT calculations, as implemented in the SIESTA code¹⁷. Core electrons are described with Troullier-Martins pseudopotentials¹⁸, while the valence wavefunction is developed over a double-zeta polarized basis set of finite-range numerical pseudoatomic orbitals.



Fig. S7. Band structure dispersion for (DicI) $MA_{n-1}Pb_nI_{3n+1}$ (n=1,4) layered halide perovskites. All compounds discussed within primitive orthorhombic frame, with plane stacking axis oriented along z. This ease the comparison between different compounds. The highlighted region is associated to interlayer band dispersion.



Fig. S8. Band structure dispersion for n=1, (DicI)PbI layered halide perovskites, with the iodine from the (DicI)²⁺ spacer substituted by a bromine (Br), a chlorine (Cl) and a hydrogen (H).

Table S4. Effective masses along the plane stacking direction for 2D $A_mMA_nPb_nI_{3n+1}$ halide perovskites containing different spacers (BA, m=2 – 3AMP, m=1 – Dicl, m=1). For Dicl spacer, we consider hypothetical compounds where the iodine from the spacer is substituted by a hydrogen, a chlorine and a iodine

spacer	n		hole	electron
BA	1		Inf.	Inf.
3AMP			0.49	1.34
Dicl		н	0.24	1.87
		Cl	0.24	1.48
		Br	0.25	1.51
		Ι	0.25	1.54
	2		0.22	0.51
	3		0.45	0.33
	4		0.43	0.23

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