Supporting Information

Phase Transitions in Low-Dimensional Layered Double Perovskites: The Role of the Organic Moieties

Beatriz Martín-García †,γ,‡,*, Davide Spirito †,γ,‡,*, Giulia Biffi †,γ,‡,*, Sergey Artyukhin †, Francesco Bonaccorso †,γ,‡,*, Roman Krahne †.

†Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova (Italy)

γCIC nanoGUNE, Tolosa Hiribidea, 76, 20018 Donostia-San Sebastian, Basque Country (Spain)

‡IHP–Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, 15236 Frankfurt (Oder) (Germany)

†Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova (Italy)

#BeDimensional S.p.A., via Lungotorrente secca 3d, 16163 Genova (Italy)

Corresponding Authors

*Beatriz Martín-García (b.martingarcia@nanogune.eu) and Davide Spirito (spirito@ihp-microelectronics.com)
Experimental Methods

Synthesis of the materials. The 3D Cs$_2$AgBiBr$_6$ crystals were prepared following the recipe from Slavney et al.$^1$ Briefly, BiBr$_3$ (112.25 mg) and CsBr (106.5 mg) were mixed and dissolved in 2.5 mL of HBr (48% vol.) at 110°C under stirring during 30 min. Then, AgBr (47 mg) was added and under stirring dissolved for 2 h, yielding an orange solution. The slow cooling of this solution to room temperature led to the formation of orange-red crystals, which were isolated by filtration on a Büchner funnel with a fritted glass disc by vacuum suction while washing with acetone. We checked the purity of the crystals by Raman spectroscopy by analyzing the frequency of the $A_{1g}$ mode.$^2$ The layered materials were synthesized adapting the recipe from Connor et al.$^3$ The (R-$\text{NH}_3$)$_4$AgBiBr$_8$ 1L crystals were growth by mixing BiBr$_3$ (102 mg), AgBr (42.5 mg) and the corresponding organic spacer (PA -75 µL, BA -90 µL, PEA -115 µL, DA-182 µL and DoA-209 µL) in 650 µL of HBr (48% vol) at 100°C under stirring during 30 min. The slow cooling of this yellow solution to room temperature led to the formation of yellow crystals, which were isolated by filtration on a Büchner funnel with a fritted glass disc by vacuum suction while washing with diethyl ether. The (R-$\text{NH}_3$)$_2$CsAgBiBr$_7$ 2L crystals were grown by mixing BiBr$_3$ (75.5 mg), CsBr (36 mg), AgBr (31.5 mg) and the corresponding organic spacer (PA -154 µL, BA -185 µL, PEA -236 µL, DA-374 µL and DoA-430 µL) in 1 mL of HBr (48% vol) at 100°C under stirring during 30 min. The slow cooling of this yellow solution to room temperature led to the formation of yellow-orange crystals, which were isolated by filtration on a Büchner funnel with a fritted glass disc by vacuum suction while washing with acetone. To allow the dissolution of DA and DoA in the reaction medium, 2 mL of toluene were added. All the collected crystals were dried inside a vial overnight (12 h) at room temperature in a Büchi® B-585 drying glass oven.
Optical characterization. The temperature-dependent absorbance spectroscopy was carried out in a Bruker Vertex 80V FT-spectrometer equipped with an Oxford Optistat liquid N₂-cryostat. Absorbance spectra at room temperature were collected using a Varian Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) and Jasco V730 UV-Vis spectrophotometer. Thin films of the materials were deposited on cleaned quartz substrates (SPI® supplies) by spin coating (3000 rpm for 40s and then 5000 rpm for 20s) solutions prepared by dissolving the crystals (~300 mg/mL in DMSO for 3D and 2L and in DMF for 1L) followed by an annealing step at 285°C (5 min), 135°C (7 min) and 100°C (4 min) for the 3D, 2L and 1L perovskites, respectively. Prior to the spin coating step, the glass substrates were cleaned in an ultrasonic bath subsequently with acetone and isopropanol (8 min each step), dried under a N₂ flow followed by a final O₂ plasma treatment (120s, 100W).

Photoluminescence spectra were collected with a Horiba i-hr320 spectrometer equipped with a Si CCD, with excitation at 325 nm (power on sample ~0.1 mW), and using a Cassegrain objective (15×, 0.28 NA). All data has been corrected by the spectral response of the system. Temperature-dependent measurements were carried out using a liquid nitrogen cryostat from Linkam®, with a quartz window for the optical access and emission collection in backscattering configuration.

Raman spectroscopy characterization. Room-temperature Raman measurements were carried out in a Renishaw® inVia equipped with a 50× (0.75 N.A.) objective with an excitation wavelength of 532 nm using a laser power < 0.1 mW, to avoid the damage of the samples during the measurement. The temperature-dependent Raman spectroscopy study was performed using a liquid nitrogen cryostat from Linkam® mounted in a Renishaw® inVia microscope equipped with a long working distance objective (50×, 0.50 NA).
**X-ray diffraction characterization.** The XRD analysis was carried out using a PANalytical Empyrean X-ray diffractometer, equipped with a 1.8 kW CuKα ceramic X-ray tube and a PIXcel3D 2x2 area detector, operating at 45 kV and 40 mA at room temperature. The crystals were deposited onto a quartz zero-diffraction single crystal substrate for the XRD measurements. The diffraction patterns were collected under ambient conditions using parallel beam geometry and symmetric reflection mode. XRD data analysis was carried out using the HighScore 4.1 software from PANalytical.

**Characterization of the materials.**

**Figure S1** includes a series of optical microscope images of the other samples under study in this work not shown in the main text, highlighting the change in the color of the crystals when replacing Cs⁺ with the alkyl and phenyl ammonium cations.

![Figure S1. Representative optical microscope images of the resulting crystals for the 2L-BA, 2L-PEA, 2L-DA, 2L-DoA (top); and 1L-BA, 1L-PEA, 1L-DA, 1L-DoA (bottom).](image)

**Evaluation of the structure.** The X-Ray diffraction patterns of all the samples involved in this study are shown in **Figure S2**. The XRD spectra of the 3D sample (Figure S2a) matches with the patterns described in the reference card (ICSD 291597) for a cubic crystal system (Fm-3m
space group) corresponding to the work of McClure et al.\textsuperscript{5} When incorporating the organic moieties to form the 2L and 1L systems, this cubic structure evolves to monoclinic (see Table S1),\textsuperscript{3,6,7} and some diffraction peaks arising from specific reflections along the $(h 0 0)$ direction start to appear in the 1L systems. From the periodicity of these diffraction peaks one can estimate the interlayer distance between the octahedral layers ($d$) displayed in Figure 1h (see main text and Table S2) between the $(\text{AgBr}_6)^5$–$(\text{BiBr}_6)^3$ octahedral layers by applying the Bragg’s law $[n\lambda = 2d \sin \theta]$, in which $n = 1$ and $\lambda(\text{Cu}) = 1.54 \text{ Å}$.\textsuperscript{8,9} The $d$ values determined by our XRD measurements agree well with the values estimated from the crystal structures built using Vesta® software\textsuperscript{10} from the crystallographic data available in literature\textsuperscript{3,6} (using ammonium alkyl chain moieties) concretely for 1L-PA, 1L-BA and 1L-OcA. The corresponding crystal structures show a crossover or entanglement of the alkyl chains when increasing the alkyl chain length (see Figure S3a). To visualize the possible arrangement of the organic moieties in 1L-DA and 1L-DoA, we sketched their crystal structures based on the 1L-OcA structure considering the $d$ value obtained from XRD, 23 Å and 20 Å, respectively. As can be observed in Figure S3b, in the case of 1L-DoA a clear crossover of the dodecylammonium moieties should occur, that would explain the shorter $d$ value in comparison with 1L-DA sample. This change in the trend of the interlayer distance is different from the monotonical increasing observed in 2D lead halide perovskites, concretely $(\text{C}_4\text{-C}_{18})_2\text{PbI}_4$, in which the crystal structure and space group is kept for the whole family of compounds.\textsuperscript{11–13} However, in the double $(\text{C}_3\text{-C}_8)_4\text{AgBiBr}_8$ perovskites studied the space group changes when the alkyl chain length varies, thus, it is possible to have a different rearrangement of the moieties leading to differences in the interlayer distance trend.
Figure S2. Representative XRD spectra of the synthesized perovskite single crystals: 3D, 2L (a) and 1L (b). The reference pattern (card ICSD 291597) for the 3D sample is also shown.

Table S1. Crystal structures and phase transitions reported in literature Cs$_2$AgBiBr$_6$ crystals and the corresponding layered structures.

| Crystal | $T_{\text{transition}}$ (K) | Crystal structure change | Technique(s) of detection | Ref.              |
|---------|-----------------------------|--------------------------|---------------------------|------------------|
| 3D      | 122                         | Tetragonal $\rightarrow$ Cubic | XRD, absorbance, heat capacity | Schade et al.$^{14}$ |
| 2L-BA   | Between 100 and 298          | Monoclinic P2$_1$/c $\rightarrow$ Monoclinic C2/m | XRD | Connor et al.$^3$ |
| 1L-BA   | Close to 298                 | Monoclinic P2$_1$ $\rightarrow$ Monoclinic P2$_1$/m | XRD | Mao et al.$^5$ |
| 2L-PA   | -                           | ? $\rightarrow$ Monoclinic P2$_1$/m | XRD | Fang et al.$^7$ |
| 1L-PA   | -                           | ? $\rightarrow$ Monoclinic C2/m | XRD | Mao et al.$^5$ |
| 1L-OcA  | -                           | ? $\rightarrow$ Monoclinic P2/m | XRD | Schade et al.$^{14}$ |
| 1L-BA   | -                           | ? $\rightarrow$ Monoclinic P2$_1$/m | XRD | Fang et al.$^7$ |
| 2L-PA   | 222                         | Monoclinic P2$_1$ $\rightarrow$ Monoclinic P2$_1$/m | XRD, differential scanning calorimetry | Zhang et al.$^{15}$ |

Table S2. Evolution of the $d$ parameter obtained from the XRD measurements for the 1L samples using different organic moieties.
| Organic moiety | PA   | BA   | PEA   | DA   | DoA  |
|---------------|------|------|-------|------|------|
| Length (Å)    | 5.5  | 6.7  | 8.4   | 14.3 | 16.8 |
| 1L d (Å)      | 11±1 | 12±1 | 16±2  | 23±2 | 20±2 |

**Figure S3.** (a) Structure of the 1L-PA, 1L-BA, and 1L-OcA crystals at room temperature plotted with VESTA software\(^1\) based on the crystallographic data from refs.\(^3\)\(^,\)\(^6\)\(^,\)\(^7\) The distance between the octahedra layers is indicated. (b) Reasonable structures of the 1L-DA and 1L-DoA crystals at room temperature built by VESTA software\(^1\) based on the \(d\) values determined by XRD and the crystallographic data from 1L-OcA in ref\(^6\).

From the crystallographic data available in the literature for 3D,\(^1\)\(^4\) 2L-/1L-PA,\(^6\) 2L-/1L-BA\(^3\) and 1L-OcA\(^6\) (see Table S1), we quantified the lattice distortion induced by the presence of the corresponding organic molecules by the mean octahedral quadratic elongation parameter (\(\lambda_{oct}\)),\(^1\)\(^6\) following the equation Eq. S1:

\[
\lambda_{oct} = \frac{1}{6} \sum_{i=1}^{6} \left( \frac{\ell_i}{\ell_0} \right)
\]  

[Eq. S1]

in which \(\ell_0\) and \(\ell_i\) are the center (Ag\(^+\) or Bi\(^{3+}\))-to-vertex (Br\(^-\)) distance in the octahedron, respectively. The center-to-vertex distances have been determined using Vesta\(^\circ\) software\(^1\)\(^0\) and the crystallographic data reported in refs.\(^3\)\(^,\)\(^6\)\(^,\)\(^7\). In this way, we evaluate the changes in the Ag-Br and
Bi-Br bond lengths with respect to the symmetric octahedron in the 3D crystal (see Table S3).
Evaluating the $\lambda_{oct}$ for both Ag and Br-containing octahedra, $(\text{AgBr}_6)^5^-$ and $(\text{BiBr}_6)^3^-$, with respect to the 3D, and using PA crystals as a representative example, we obtain: 3D ($\lambda_{\text{Ag-Br}}=\lambda_{\text{Bi-Br}}=1$), 2L-PA ($\lambda_{\text{Ag-Br}}=1.022$ and $\lambda_{\text{Bi-Br}}=1.011$) and 1L-PA ($\lambda_{\text{Ag-Br}}=1.048$ and $\lambda_{\text{Bi-Br}}=1.013$). Here, the stronger distortion occurs in the $(\text{AgBr}_6)^5^-$ octahedron, as was also pointed out by Connor et al. for 2L-BA and 1L-BA.³ Comparison with the values of Connor et al.³ reveals that the length of the organic spacer also plays a role, since for the BA moieties a stronger distortion is observed: 2L-BA ($\lambda_{\text{Ag-Br}}=1.034$) and 1L-BA ($\lambda_{\text{Ag-Br}}=1.072$). The structural data provided by Connor et al.³ indicates changes in the octahedral tilt pattern in the inorganic layer with increasing temperature, as shown for the 1L-BA crystal in Figure S4 (prepared using Vesta software¹⁰), in which the angles between the successive octahedra $(\text{AgBr}_6)^5^-/(\text{BiBr}_6)^3^-/(\text{AgBr}_6)^5^-$ in the same layer defined by the Bi-Br-Ag bonds vary from 186° to 163° when passing from 100 K to 298 K.

Table S3. Ag-Br and Bi-Br bond distortion in terms of the mean octahedral quadratic elongation parameter ($\lambda_{oct}$) for the $(\text{AgBr}_6)^5^-$ and $(\text{BiBr}_6)^3^-$ octahedra for different organic cations in the 2L and 1L crystals compared to the 3D counterpart.

| Crystal | $\lambda_{\text{Ag-Br}}$ | $\lambda_{\text{Bi-Br}}$ |
|---------|-------------------|-------------------|
|         | T<T transition | T>T transition | T<T transition | T>T transition |
| 3D      | 1                | 1                | 1               | 1                |
| 2L-PA   | -                | 1.022            | -               | 1.011            |
| 1L-PA   | -                | 1.048            | -               | 1.013            |
| 2L-BA   | 1.038            | 1.034            | 1.022           | 1.017            |
| 1L-BA   | 1.058            | 1.072            | 1.026           | 1.017            |
| 1L-OcA  | -                | 1.029            | -               | 1.005            |
Figure S4. Structure of the 1L-BA crystal at $T = 100$K and $T = 298$K visualized with VESTA 3 software based on the crystallographic data from ref. 3.

Figure S5a-b shows the Raman spectra in the 100-300 cm$^{-1}$ range at room temperature, which reveal a systematic red shift of the $A_{1g}$ Raman mode, when the system changes from 3D (176±2 cm$^{-1}$, in agreement with literature$^{2,17,18}$) to 2L and to 1L materials. Mechanically exfoliated (Scotch tape) 2L or 1L samples on silicon wafers (90 nm thermal SiO$_2$, Ti/Au markers defined by direct laser-writer using a DWL 66FS, Heidelberg Instruments Mikrotechnik GmbH) are depicted in Figure S5c, as thin blue-white colored flakes. The observed Raman modes did not show any dependence on the thickness of the flakes, indicating that the position of the Raman modes only depends on the crystal structure, but not on the thickness of the crystal.
Figure S5. (a) Representative Raman spectra (532 nm excitation wavelength) of the 3D, 2L and 1L crystals in the 100-300 cm$^{-1}$ range. (b) Position of the A$_{1g}$ mode in the Raman spectrum for the different systems, showing a dependence on the length of the alkyl chain or phenyl group. The star symbols indicate values from the literature for the 3D crystal, refs$^{2,17,18}$. (c) Raman spectra collected on exfoliated 2L-BA (left graph-bottom image) and 1L-BA (right graph-top image) thin flakes that appear in different colors in the microscope images. The colored dots indicate the measurement spots in the optical microscope images.

Additional Raman spectroscopy data of 3D, PA, BA, PEA, and DA samples

The Raman spectra at different temperatures in the range 80 – 350 K in the 100-250 cm$^{-1}$ spectral range for the 3D, PA, BA, PEA, and DA samples are shown in (a) panels of Figures S6-S9,
respectively. The position and FWHM of the Raman peak associated to the $A_{1g}$ mode is depicted in the (b) panels.

**Figure S6.** (a) Representative Raman spectra in the 100-250 cm$^{-1}$ region for 3D, 2L-PA and 1L-PA at selected temperatures, respectively. (b) Temperature evolution of the $A_{1g}$ mode frequency (top panel) and FWHM (bottom panel). Full symbols indicate the data acquired during heating from base temperature, while empty ones during cool down.

**Figure S7.** (a) Representative Raman spectra in the 100-250 cm$^{-1}$ region for 2L-BA and 1L-BA at selected temperatures, respectively. (b) Temperature evolution of the $A_{1g}$ mode frequency (top panel) and FWHM (bottom panel). Full symbols indicate the data acquired during heating from base temperature, while empty ones during cool down.
Figure S8. (a) Representative Raman spectra in the 100-250 cm\(^{-1}\) region for 2L-PEA and 1L-PEA at selected temperatures, respectively. (b) Temperature evolution of the \(A_{1g}\) mode frequency (top panel) and FWHM (bottom panel). Full symbols indicate the data acquired during heating from base temperature, while empty ones during cool down.

Figure S9. (a) Representative Raman spectra in the 100-250 cm\(^{-1}\) region for 2L-DA and 1L-DA at selected temperatures, respectively. (b) Temperature evolution of the \(A_{1g}\) mode frequency (top panel) and FWHM (bottom panel). Full symbols indicate the data acquired during heating from base temperature, while empty ones during cool down.
Figure S10. Raman modes of the organic moieties for the 1L systems at different temperature. Representative Raman spectra in the 1100-1650 cm\(^{-1}\) (left) and 2800-3200 cm\(^{-1}\) (right) regions for 1L-PA (a) at selected temperatures: 98, 200 and 298 K; for 1L-BA (b) at 98, 273 and 300 K and 1L-PEA (c) at 98,
200 and 298 K, showing the vibrational modes of the propylammonium, butylammonium and phenylethylammonium cations, respectively. (c) Notation used: δ, stretching; β, bending; τ, twisting; ω, wagging, and ν, other vibrations.

Figure S11. Raman modes of the organic moieties for the PA and BA 2L systems at different temperature. Representative Raman spectra in the 1100-1650 cm\(^{-1}\) (left) and 2800-3200 cm\(^{-1}\) (right) regions for 2L-PA (a) at selected temperatures: 93, 198 and 298 K and for 2L-BA (b) at 98, 273 and 298 K, showing the vibrational modes of the propylammonium and butylammonium cations, respectively. Notation used: δ, stretching, β, bending; τ, twisting; ω, wagging, and ν, other vibrations.

Additional absorbance and photoluminescence spectroscopy characterization

As in the graphs shown in the main text for 3D and 2L/1L-PA (Figure 4a), in the absorbance spectra of the films prepared from the 2L/1L-BA and 2L/1L-PEA systems, only a slight absorption peak broadening with increasing temperature is observed, see Figure S12.
Figure S12. Normalized temperature-dependent absorbance spectra intensity maps for 2L/1L-BA and 2L/1L-PEA films. The dashed line indicates the absorption peak position.

However, in the absorbance spectra at room temperature, displayed in Figure S13, a systematic blue shift in the absorption peak position is observed when replacing the Cs\(^+\) with the alkyl and/or phenyl ammonium cations in the Cs\(_2\)AgBiBr\(_6\) perovskite structure towards 2L or 1L together with the organic spacer length, from 3D (2.84 eV, 436 nm) to 2L (2.92 eV, 425 nm) to 1L (2.99 eV, 415 nm) in line with published results\(^3\). Therefore, the structural change from 3D to 2L or 1L is also highlighted in the optical properties of the material.
**Figure S13.** (a) Representative absorbance spectra of the films prepared from the synthesized perovskite single crystals: 3D, 2L and 1L. (b) Absorption peak position change with the introduction of the organic spacer in the perovskite structure. Average values from 3 different films for each sample. For comparison, values from the literature, ref^3 are included as star symbols.

* Urbach tail analysis of the absorption coefficient slope: We carried out a linear fit of the logarithmic of the absorption coefficient (α) with the photon energy (E) in the range of temperatures (T) under study by means the Urbach rule: \( \alpha(E) = \alpha_0 e^{-\frac{E_0 - E}{k_B T}} \); concretely ln(α) vs E, see **Figure S14**, to determine if the linear fits converge to a single point corresponding to (E₀, \( \alpha_0 \)) that allows to estimate the optical bandgap (see **Table S4** for the values, when crossing, namely at high temperatures).^3,19,20 We obtain similar results for the optical bandgap from this analysis of the temperature-dependent absorption coefficient and directly from the peak position in the absorption.
Figure S14. Representative examples of the linear fit obtained from the analysis of the logarithmic of the absorption coefficient (α) with the photon energy (E) for the following samples: 3D, 2L/1L-PA and 1L-BA.

Table S4. Values of the estimated optical bandgap by Urbach tail analysis for several samples.

| Sample | abs peak (eV) | $E_0$ (eV) | crossing above T (K) |
|--------|--------------|------------|----------------------|
| 3D     | 2.83         | 2.65       | 248                  |
| 2L-PA  | 2.85         | 2.70       | 248                  |
| 2L-BA  | 2.92         | 3.15       | 248                  |
| 2L-PEA | 2.94         | 2.80       | 248                  |
| 1L-PA  | 2.95         | 2.90       | 223                  |
| 1L-BA  | 2.99         | 2.83       | 288                  |
| 1L-PEA | 2.97         | 2.85       | 248                  |

Complementary PL data: Representative temperature dependent PL spectra for 2L/1L-BA and 2L/1L-PEA samples is shown in Figures S15-S16.
Figure S15. Representative photoluminescence spectra together with the evolution of the PL peak intensity and FWHM for 2L-BA (a) and 1L-BA (b) in the 80 – 350 K range.

Figure S16. Representative photoluminescence spectra together with the evolution of the PL peak intensity and FWHM for 2L-PEA (a) and 1L-PEA (b) in the 80 – 350 K range.

Evaluation of the electron-phonon coupling and Stokes shift. Another important aspect to evaluate combining the information from Raman spectroscopy and the optical properties of the crystals is the interaction between phonon modes and optical centers, which can be characterized by the Huang-Rhys factor \( S \).\(^{17} \) This factor relates the Stokes shift energy \( \Delta E_{\text{Stokes}} \) and the LO phonon energy \( \hbar \omega_{\text{LO}} \), in our case related to A\(_{1g} \) mode) as \( \Delta E_{\text{Stokes}} = 2 S \hbar \omega_{\text{LO}} \). In Table S5 we summarize the values for absorption peaks \( E_{\text{abs}} \) and PL peaks \( E_{\text{PL}} \) that are almost constant in
the temperature range investigated (80-350K), Raman modes ($\hbar\omega_{LO}$) at low (80K) and room temperature, and evaluate the $(\Delta E_{Stokes}=E_{PL}-E_{abs})$ and the Huang-Rhys parameter $S=\Delta E_{Stokes}/(2\hbar\omega_{LO})$ for the samples used in the PL study. We obtained large Huang-Rhys values for 3D (S ~ 19, in line with reported data: 12 for Zelewski et al.\textsuperscript{17} – 15.4 for Steele et al.\textsuperscript{2}) and 2L crystals (S ~ 22), confirming strong electron-phonon interactions, while small values for the 1L crystals (S ~ 1) were obtained, in accordance with a direct bandgap.

Table S5. Values of the Huang-Rhys factor obtained at 80 K and RT from the absorption, PL peak and Stokes shift for several samples.

| Sample | abs peak (eV) | PL peak (eV) | Raman @ 80K (eV) | Raman @ RT (eV) | Stokes shift (eV) | Huang-Rhys factor, S @ 80K | Huang-Rhys factor, S @ RT |
|--------|--------------|--------------|------------------|----------------|------------------|---------------------------|--------------------------|
| 3D     | 2.85         | 1.97         | 0.0222           | 0.0218         | 0.86             | 19.4                      | 19.7                     |
| 2L-PA  | 2.85         | 2.04         | 0.0218           | 0.0212         | 0.81             | 18.6                      | 19.1                     |
| 2L-BA  | 2.92         | 1.98         | 0.0215           | 0.0211         | 0.94             | 21.9                      | 22.3                     |
| 2L-PEA | 2.94         | 1.99         | 0.0199           | 0.0197         | 0.95             | 23.9                      | 24.1                     |
| 1L-PA  | 2.95         | 2.93         | 0.0201           | 0.0202         | 0.02             | 0.5                       | 0.5                      |
| 1L-BA  | 2.99         | 2.93         | 0.0197           | 0.0200         | 0.06             | 1.5                       | 1.5                      |
| 1L-PEA | 2.97         | 3.00         | 0.0198           | 0.0197         | 0               | 0                         | 0                        |

Computational details

First-principles calculations have been carried out using SIESTA\textsuperscript{21} and Quantum Espresso\textsuperscript{22} codes with PBEsol exchange-correlation functional\textsuperscript{23} and relativistic optimized norm-conserving Vanderbilt (ONCV) pseudopotentials generated by D. Hamann’s code\textsuperscript{24} and available at pseudo-DOJO\textsuperscript{25}. Crystallographic structures of both BA- and PA-based compounds with single (1L) and double (2L) inorganic layers were retrieved from literature,\textsuperscript{3,6} as well as the crystal structures below and above the transition temperature for BA-based crystals\textsuperscript{3}. For the cases in which multiple orientations of organic moieties were reported, we have only retained one of them and performed a structural optimization of the molecules. We kept the unit cell geometry and inorganic ions fixed, to make sure that the optimization of the alkyl chain conformation does not affect the octahedral
tilt pattern in the inorganic layers. All the simulations have been carried out using the SIESTA code, and including spin-orbit coupling. Reference calculations with a plane-wave code (Quantum Espresso) were performed to validate the basis set and convergence parameters used in SIESTA. Inclusion of spin-orbit coupling (SOC) is of utmost importance to reproduce the band structure, due to the presence of Bi$^{3+}$ ions, whose contribution dominates the lowest conduction bands. If spin-orbit coupling is neglected, the 1 eV splitting of the lowest conduction bands is not captured (Figure S17a,b).

![Band structure and projected density of states](image)

**Figure S17.** Band structure and projected density of states of (a) 1L-BA at 100K without spin-orbit coupling and (b) 1L-BA at 100K with spin orbit coupling (also shown in Figure 5a of the main text). The inclusion of the spin-orbit coupling turns the indirect bandgap into a direct one for 1L compounds.

In the main text, we provided the comparison between 1L-BA and 1L-PA, that shows no major differences in their band structures in the room-temperature structures. Similarly, no major differences are present between the band structures of 2L-BA and 2L-PA (Figure S18a, b), further suggesting that while a variation in the organic chain length might affect the transition temperature, it does not considerably influence the bands across the gap and the optical properties of these compounds. Consistently with ref.3, the bandgap is indirect in 2L samples.

For completeness, the study of the electronic properties at different temperatures was performed also on 2L-BA. The results are similar to those reported for the 1L structures, in agreement with the experimental data (Figure S18a, Figure 5b in the main text).
**Figure S18.** Band structure and projected density of states of (a) 2L-BA at 298K, (b) 2L-PA at 298K, (c) 2L-BA at 298K after geometry relaxation and (d) 1L-BA with undistorted octahedra.

The band structure computed using 2L-BA room temperature structure (with one particular molecular conformation chosen out of multiple atomic positions given in ref.3) without geometry relaxation shows a flat band originating from carbon 2p-orbitals intersecting the top valence band. Geometry optimization moves this flat band to lower energies, suggesting this band to be an artefact due to the molecular geometry taken arbitrarily from multiple average positions in the room temperature XRD, being far from the equilibrium conformation of the chain itself (Figure S18c). Figure S18d shows the band structure and the density of states (DOS) computed for a fictitious structure with octahedral tilts removed: band degeneracies appear at the Brillouin zone boundary in line with the higher symmetry, but the bands across the gap are largely similar to the ones computed using experimental structures. The symmetry of this structure is Cmmm (#65 in International Tables26). The flatness of the conduction band can lead to very interesting phenomena: for example, applying a ferroelectric mode, such as Γ2+, with amplitude as small as
1:10 of that of $\Gamma_3^+$, the one already present at room temperature that causes the out-of-plane tilting of the octahedra, produces a shift in the position of the minimum of the conduction band, thus making the bandgap indirect (Figure S19b).

**Figure S19.** (a) Density of the Bi-centered Wannier function for the lowest conduction band of 1L-BA at low-temperature that does not hybridize with high energy Ag orbitals, resulting in a wavefunction localization on Bi and Br atoms and a flat conduction band. (b) Band structure and projected density of states of the 1L-PA structure at room temperature with a small ferroelectric $\Gamma_2^+$ mode applied. The red asterisk marks the minimum of the conduction band.

**References:**

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