Uniaxial Expansion of the 2D Ruddlesden–Popper Perovskite Family for Improved Environmental Stability

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Supporting Information

ABSTRACT: The unique hybrid nature of 2D Ruddlesden–Popper (R–P) perovskites has bestowed upon them not only tunability of their electronic properties but also high-performance electronic devices with improved environmental stability as compared to their 3D analogs. However, there is limited information about their inherent heat, light, and air stability and how different parameters such as the inorganic layer number and length of organic spacer molecule affect stability. To gain deeper understanding on the matter we have expanded the family of 2D R–P perovskites, by utilizing pentylamine (PA)$_2$(MA)$_{2n-1}$Pb$_{1n+1}$ (n = 1–5, PA = CH$_3$(CH$_2$)$_5$NH$_3$+, C$_5$) and hexylamine (HA)$_2$(MA)$_{2n-1}$Pb$_{1n+1}$ (n = 1–4, HA = CH$_3$(CH$_2$)$_4$NH$_3$+, C$_6$) as the organic spacer molecules between the inorganic slabs, creating two new series of layered materials, for up to n = 5 and 4 layers, respectively. The resulting compounds were extensively characterized through a combination of physical and spectroscopic methods, including single crystal X-ray analysis. High resolution powder X-ray diffraction studies using synchrotron radiation shed light for the first time to the phase transitions of the higher layer 2D R–P perovskites. The increase in the length of the organic spacer molecules did not affect their optical properties; however, it has a pronounced effect on the air, heat, and light stability of the fabricated thin films. An extensive study of heat, light, and air stability with and without encapsulation revealed that specific compounds can be air stable (relative humidity (RH) = 20–80% ± 5%) for more than 450 days, while heat and light stability in air can be exponentially increased by encapsulating the corresponding films. Evaluation of the out-of-plane mechanical properties of the corresponding materials showed that their soft and flexible nature can be compared to current commercially available polymer substrates (e.g., PMMA), rendering them suitable for fabricating flexible and wearable electronic devices.

INTRODUCTION

The broad class of hybrid halide perovskites AMX$_3$ (A = Cs+, CH$_3$NH$_3$+ (MA), HC(NH$_2$)$_2$– (FA)); M = Ge$^{2+}$, Sn$^{2+}$, Pb$^{2+}$; X = Cl$^-$, Br$^-$, I$^-$) in solid state solar cells has received huge scientific attention because of the highly promising performance of the corresponding assembled devices as well as the beneficial electronic properties of these direct band gap semiconductors. The power conversion efficiencies (PCEs) of perovskite-based devices that have been achieved so far (>23%) meet or exceed those of current market available materials, paving the path for their potential commercialization. Although the performance of hybrid halide perovskites is comparable (but mechanistically different) to that of their major solar absorber competitors (Si, GaAs), there are a number of obstacles that hinder the entrance of these materials to the market, with the most important being inadequate environmental stability. A solar cell module has to be air, light, and heat stable, withstanding fluctuations in these parameters over a very wide time period.

Recent studies evaluating the life-cycle environmental impact of perovskite/silicon tandem modules, containing lead-based hybrid halide perovskites, show that the emitted lead contributes only 0.27% or less to the total freshwater ecotoxicity and human toxicity, as compared to the other solar
module components.14 These encouraging results clearly indicate that the remaining hindrance to be overcome is the environmental stability of the perovskite-absorbing layer.

Previously, we and others have shown that 2D perovskites (e.g., $A_xA_{1-x}M_xX_{2n+1}$)5 where $A'$ is a monovalent or divalent organic cation15 acting as a spacer between the perovskite layers, $A = $ monovalent cation, e.g., Cs+, CH$_3$NH$_3$+, HC-(NH$_2$)$_2$+, M = $M_x$+, Sn$^{2+}$, Pb$^{2+}$; $X = $ CI−, Br−, I−) tend to have superior stability than 3D perovskites.17–19 This can be achieved by introducing, during the synthesis of the 3D perovskites (e.g., MAPbI$_3$, $A$ = CH$_3$NH$_3$+, of organic molecules containing amine groups that can act both as spacers between the inorganic layers and as charge-balancing cations of the structure.20 The ability to utilize organic spacer molecules of diverse chemical nature leads to materials with attractive properties, one of them being improved moisture and potentially improved heat and light stability.19

Although there are numerous reports mentioning the environmental stability of mixed phase 2D/3D halide perovskite films and solar cells such as PEA$_2$PbI$_4$/C$_8$H$_{16}$FA$_{0.5}$MA$_{0.5}$PbI$_{3.5}$Br$_{0.5}$ (PEA = $C_6$H$_5$(CH$_2$)$_2$NH$_3$+, (HOOC(CH$_2$)$_2$NH)$_2$Pb$_4$/MAPbI$_3$, (CA$_2$Pb$_4$/MAP-bI$_3$Cl$_{1-n}$), (CA$_2$): cyclopentylamine)23 doped 3D materials with bulky organic cations such as BA-FAPbI$_3$ (BA = CH$_3$(CH$_2$)$_5$NH$_3$+, C6). For simplicity the notation C$_5$N$_4$(MA)$_{3-n}$Pb$_{13}$ is used here for the first time, with chemical formulas (PA)$_2$(MA)$_{n-1}$Pb$_{13n-1}$ (n = 1–5), PA = CH$_3$(CH$_2$)$_4$NH$_3$+, C5 and (HA)$_2$(MA)$_{n-1}$Pb$_{13n-1}$ (n = 1–4), HA = CH$_3$(CH$_2$)$_5$NH$_3$+, C6. For simplicity the notation CSN1–5 and C6N1–4 is used throughout this work, where the number after the (C) corresponds to the number of carbon atoms of the side organic chain and the number after (N) corresponds to the number of the inorganic layers (i.e., layer thickness). The resulting materials were extensively characterized with single-crystal XRD and powder XRD (PXRD) studies. High-resolution variable-temperature PXRD measurements using synchrotron radiation verified the phase transition temperature of these perovskites, which were consistent with DSC measurements. TGA analysis shed light on the thermal stability of the crystals, while UV–vis spectroscopy, photoluminescence (PL), and TRPL measurements evaluated the optical properties of these compounds. Ambient-pressure photoemission spectroscopy (APS) was used for experimental determination of the valence band maximum of the crystals, allowing accurate determination of the band structures.

Following the characterization of the new 2D perovskite materials we evaluated their environmental (heat, light, and air) stability by performing an extensive series of tests with and without encapsulation and compared it to the previously reported compound based on butylamine as well as their 3D counterpart, MAPbI$_3$. In order for these studies to be as close as possible to commercial device applications we fabricated thin films of these perovskites on different substrates (amorphous glass, crystalline SiO$_2$, and polycrystalline Si) and used them for the stability tests. Two different film-casting methods were used (one step (OS) and hot casting (HC)) as well as different film concentrations to cover a wider range of experimental parameters. The new compounds exhibit improved thermal (4 h at 100 °C, for CSN4) and light stability (10 h continuously under 1 sun illumination, for CSN5) in air, as compared to the previously reported 2D analogue (C4N4), and much higher than the 3D analogue (MAPbI$_3$) which...
contained a significant amount of PbI₂ treated under identical conditions. At the same time, most of the materials maintain their structural integrity in air and desired orientation for more than a year, depending on the used substrate and casting method (CSN3 on polycrystalline (100) Si). Interestingly, if the corresponding thin films are encapsulated (protected from moisture and O₂) then their heat (12 days at 100 °C in air, for CSN4, 90 days continuously in the glovebox for CSN3) and light (60 h under 1 sun illumination in air, for CSN4) stability is dramatically increased as compared to the unencapsulated ones. This finding is especially important as it may offer a potential solution to their inherent heat and light instability under ambient conditions, which is obsolete if the films are sufficiently protected from air. Lastly, we evaluated the bulk mechanical properties of the resulting crystalline materials by measuring the Young’s modulus and hardness. Apparently, by increasing the side carbon chain length of the spacer molecules, one can adjust the softness of the material. These measurements provide insight for the potential utilization of those materials not only in static large solar cell assemblies but also in flexible and wearable electronic devices, an unexplored but potentially fruitful field for the perovskite materials.

## RESULTS AND DISCUSSION

We first discuss the synthetic aspects of this family of materials and describe their refined crystal structures, thermal analysis, and temperature-induced phase transitions. We then present their optical absorption and photoluminescence properties and study of their mechanical properties. Finally, we present the film assembly process, which gives uniform highly oriented films, which were used for systematic investigation of their temporal stability under a broad set of environmental conditions.

### Synthetic Aspects

Both new families of 2D perovskites (PA)₁ₓ(MA)₁−ₓ−nPbI₃ₓ₁ for the (BA)₁ₓ(MA)₁−ₓ−nPbI₃ₓ₁ and (HA)₁ₓ(MA)₁−ₓ−nPbI₃ₓ₁ were synthesized using a HI/H₃PO₄ solvent mixture, which can produce uniform and high-quality single crystals. One would expect that since the difference of those materials with the previously published ones, (BA)₁₋ₓ(MA)ₓ−nPbI₃ₓ₁, is only one and two carbon atoms using PA and HA, respectively, the optimum reaction conditions would be if not identical at least almost the same. However, the resulting synthetic parameters, such as the organic spacer and reactants concentration, varied significantly with increasing the carbon chain length of the organic spacer molecule. In the case of PA and HA analogs, the synthetic procedure was simplified, both by the use of much cheaper starting materials, such as PbO and MACl, instead of PbI₂ and MAI, and by the modification of the reaction steps. Initially, the same amount of PbO (10 mmol) was dissolved under heating in a suitable amount of solvent (16 and 17 mL of HI for PA and HA, respectively), then a stoichiometric amount of MACl was added, leading to formation of the 3D analogue (MAPbI₃) that was fully dissolved, and then the optimum spacer concentration was added to the H₃PO₄ solution at room temperature (RT). Because of the milder reaction of the amine with the H₃PO₄ compared to the highly exothermic reaction with the HI acid in the case of synthesis of the BA analogs, use of an ice bath is not needed, simplifying the reaction conditions. Lastly, the H₃PO₄ solution with the spacer is added to the hot reaction slowly, and the clear yellow solution is left to cool slowly at RT. If the solution is cooled immediately at RT then a mixture of products, containing different number of inorganic layers, is formed. This clearly indicates the delicate nature of the crystallization process of these hybrid materials, where the system needs time to arrange in the solution all of the different reaction components for the acquisition of only one thermodynamically stable phase.

In targeting a specific layer thickness (e.g., (PA)₁₋ₓ(MA)ₓ−nPbI₃ₓ₁ = CSN4) the following general synthetic strategy was developed and implemented in all cases. The stoichiometric ratio Pb/MA, based on the chemical formula, was utilized, and the concentration of PA was varied until a product of a uniform layer number was obtained. Interestingly, although the targeted material was in this example the CSN4, based on the stoichiometric ratio of Pb/MA (4:3), the resulting products were determined by the amount of PA spacer, starting from CSN2 (80% main product) for the highest amount of PA, to the CSN5 for the lowest amount, see Figure S2. After the optimum amount of spacer for each number of layers was determined experimentally, a second set of experiments was carried out. In this case the amount of spacer was fixed, targeting, e.g., the CSN4, and the ratio Pb/MA was modified targeting different number of layers, e.g., 5, 6, and 7. As it is shown in Figure S3, the resulting material in all cases was the CSN4, governed by the specific amount of spacer only. In the final round, after determining the optimum amount of spacer for each specific number of layers, the stoichiometric Pb/MA ratio was used, targeting each number of inorganic layers, which led to the synthesis of pure, uniform layer compounds. These results clearly indicate that the critical parameter toward acquiring a pure product is the concentration of spacer in solution and to a much lesser degree the Pb/MA ratio. The same trend was also observed in the case of HA. Notably, for the same amount of Pb²⁺ cations (10 mmol) the optimum amount of spacer (BA, PA, HA) decreases with increasing the length of the organic chain (see Figure S4), and also the overall concentration of the reactants decreases (by increasing the amount of the HI solvent) because of the decrease of the solubility of the resulting materials.

In Figure S4 we present the dependence of the spacer concentration toward the number of layers for all 3 families of materials, based on BA, PA, and HA. In all cases the same trend is observed regarding the concentration of spacer with increasing number of layers, where it reaches a plateau for n > 5. This clearly indicates the synthetic challenge in the acquisition of pure, n > 5 materials, as the difference in the optimum concentration for high layers is small. Furthermore, considering these trends, it is possible to estimate the optimum concentration of spacer for specific materials based on spacer molecules with longer or shorter organic chains. This tailor-made synthetic methodology, presented here for the first time in these compounds, can be a unique and general tool for further expansion of the 2D perovskite family.

### Structural Properties

Single-crystal XRD analysis revealed that the resulting materials (7 solved single-crystal structures, 6 of them new) (PA)₁₋ₓ(MA)ₓ−nPbI₃ₓ₁ and (HA)₁₋ₓ(MA)ₓ−nPbI₃ₓ₁ belong to the 2D Ruddlesden–Popper perovskite family, and they constitute a uniaxial expansion of the previously reported (BA)₁₋ₓ(MA)ₓ−nPbI₃ₓ₁ compounds along the layer stacking axis. Room-temperature PXRD measurements verified the phase purity of the synthesized materials, as there are no residual low-angle peaks (<13° 2θ) which would be an indication of coprecipitation of more than one inorganic layer in each case (see Figure 1). Furthermore, comparison of the calculated PXRD patterns based on the
C6N1, and C5N2 materials have been presented before;39,40 as in the case of the 3D perovskites.42 Cations reside into the cavities formed by the inorganic chains) and electrostatic interactions (between the ammonium molecules the distance between the inorganic layers increases from 7.0 Å for the BA compounds to 8.5 and 9.4 Å for the PA and HA, respectively (without taking into account the van der Waals radii).43 The BA-based 2D perovskites crystallize in monoclinic space groups. Taking a closer look at the upper axial Pb−I bond lengths of the octahedra of the outer inorganic layers (those facing the organic layer), for n = 4 the distance varies from 3.044(2) to 3.069(4) and 3.050(4) Å for the BA, PA, and HA analogs, while the lower axial Pb−I distances vary from 3.3091(18) to 3.302(4) and 3.217(5) Å, respectively, thus progressively decreasing the polarity of the layers along the confinement direction.

Regarding the (Pb−I−Pb)011 in-plane equatorial tilting angles, in the case of (PA)2+(MA)n−1PbI3n+1 series (n = 2−5) there is a slight decrease with increasing n, with values of 162.32(9)°, 164.12(6)°, 162.98(14)°, and 161.4(2)° for CSN2, CSN3, CSN4, and CSN5, respectively. This trend is almost ironed out by calculating the average Pb−I−Pb angles (axial and equatorial) which exhibit values of 163.1°, 165.1°, 164.3°, and 163.2°, respectively. For the (HA)2+(MA)n−1PbI3n+1 series (n = 2−4), the corresponding average values range from 167.6° to 165.2° and 163.4° for C6N2, C6N3, and C6N4, respectively. Additionally, there is not a clear trend in the (BA)2+(MA)n−1PbI3n+1 perovskite series also (n = 2−5) with values of 164.9°, 170.7°, 169.2°, and 165.4° for the C4N2, C4N3, C4N4, and C4N5 materials, respectively. These findings indicate that with increasing thickness of the inorganic layers (i.e., value of n) there is only a small impact from the organic spacer molecules toward the distortion of the perovskite structure, as it was also observed in the case of the isostructural 2D hybrid Dion−Jacobson perovskites (3AMP)(MA)n−1PbI3n+1 and (4AMP)-(MA)n−1PbI3n+1 (3AMP = 3-(aminomethyl)piperidinium, 4AMP = 4-(aminomethyl)piperidinium).44 These observations support the trend in the optical properties of the three different homologous perovskite families described here (see below).

All (PA)2+(MA)n−1PbI3n+1 and (HA)2+(MA)n−1PbI3n+1 compounds crystallize in monoclinic space groups at room temperature (Table 1), except for C6N1, which crystallizes in an orthorhombic space group.45 This is verified by the comparison of the calculated and experimental PXRD patterns.
reported one by Billing et al.\textsuperscript{39} As the value of the transition temperature starts at 47 °C, from the DSC measurements it was possible to identify the thinnest layer analogues, and then for the C5N3, C5N4, and C5N5 materials the temperature remains almost the same with values of 80 and 103 °C, respectively (Figure 4a). The other hand, for the (HA)\textsubscript{2}(MA)\textsubscript{1−n}PB\textsubscript{1−1.1} compounds are orthorhombic at RT.\textsuperscript{18} While all (BA)\textsubscript{2}(MA)\textsubscript{n}PB\textsubscript{1−1.1} compounds are orthorhombic at RT.

Temperature-dependent phase transitions are a common phenomenon in hybrid halide perovskites, not only in the thinner layer 2D C5N1, C6N1, C7N1, and C12N1 perovskites,\textsuperscript{32,45,46} but also in the case of the 3D analogs MAPbI\textsubscript{3}, FAPbI\textsubscript{3}, and MA(SnCl\textsubscript{3}). Therefore, it is likely that in the case of higher layer (n > 1) Ruddlesden–Popper hybrid perovskites a similar behavior is observed. To verify this we performed high-resolution variable-temperature PXRD as well as differential scanning calorimetry (DSC) measurements. From the DSC measurements it was possible to identify the exact temperature of the phase transitions occurring above RT. For the (PA)\textsubscript{2}(MA)\textsubscript{n−1}PB\textsubscript{1−1.1} material of families of materials the transition temperature starts at 47 °C, heating cycle, for the lowest n member compound C5N1, close to the previously reported one by Billing et al.\textsuperscript{39} As the value of n is increased, the transition temperature increases to 78 °C for the C5N2 analogue, and then for the C5N3, C5N4, and C5N5 materials the temperature remains almost the same with a range of 80 and 103 °C, respectively (Figure 4a).

**Table 1. Crystal and Structure Refinement Data for CSN2−5 and C6N2−4 Compounds\textsuperscript{a}**

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**Figure 4.** (A) DSC curves for all CSN1−5 materials and (B) C6N1−4 recorded under helium flow. The small peak of sample C6N1 (at 97 °C) is not an C6N2 impurity, as there is no methylammonium cations in the synthesis that could lead to the formation of the two layered structure and is consistent to what was observed before. Corresponding sharp endothermic peaks are indicative of the phase transition temperature of these materials.

DSC peak at 82 and 97 °C, in perfect agreement with the previously reported ones at 81.7 and 98.1 °C, respectively.\textsuperscript{39} However, with increasing layer thickness there is only one transition which shifts to higher temperatures, starting at 96 °C for the C6N2 material, 103 °C for the C6N3 material, and 123 °C for the C6N4 material (Figure 4b).

There are two trends stemming from the above analyses, with the first one being that the phase transition temperature depends on the organic spacer but does not follow a specific
order. For the \((\text{PA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) series the temperature ramps up to \(\sim 80^\circ\text{C}\) and remains nearly constant irrespective of \(n\) while in \((\text{HA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) the transition temperature increases in a stepwise manner showing a strong dependence on the \(n\) number. For \((\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\), the phase transitions appear to be closer to the trend observed for \((\text{PA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) with all end members converging to a phase transition at \(\sim 10^\circ\text{C}\). Unlike the trend observed for longer organic chains analogs, the premelting phase transition was not observed in the studied homologous series.\(^{52}\) The second trend is that the phase transition temperature increases with increasing layer thickness in \((\text{PA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) and \((\text{HA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\), unlike \((\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) where the transition temperature is nearly constant. These observations can be explained by the fact that during a phase transition adjacent inorganic layers shift relative to each other, as the organic molecules adopt a different orientation, followed by a tilting of the inorganic octahedra, as recorded for the C5N1 and C6N1 compounds.\(^{39}\)

High-resolution variable-temperature PXRD measurements using synchrotron radiation (11BM) confirmed the trends and transition temperatures of the DSC results. In the case of C5N1 and C6N1 the materials crystallize in a monoclinic \((P2_1/\alpha)\) and in an orthorhombic \((Pbc\alpha)\) space group, respectively, as the experimental RT PXRD patterns (recorded in-house) match exactly the calculated ones from the single-crystal XRD measurements (see Figures S5 and S10). Regarding the \((\text{PA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) \((n = 2−4)\) series, all materials undergo a phase transition between 70 and 90 °C (C5N2–4), in agreement with the DSC phase transition temperatures \((78−81^\circ\text{C})\) (Figures 4, S15, and S16). The recorded PXRD patterns at 70 °C are the same as the RT measured ones, while above 80 °C, the corresponding patterns shift and shrink to lower 2\(\theta\) values, followed by disappearance of the \((400)\) peak of the monoclinic phase and appearance of the \((080)\) peak of the orthorhombic phase (see Figure 5). At 69 °C in the cooling cycle PXRD pattern, the phase transformation exhibits a hysteresis, as both phases exist simultaneously, which is evident by the presence of both characteristic \((400)\) and \((080)\) peaks (see Figures 5 and S15 and S16). All phase transitions were fully reversible in the examined temperature range \((29−180^\circ\text{C})\), as the initial and the final target temperature diffraction patterns match exactly.

Similar results were also observed in the \((\text{HA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) \((n = 2−4)\) series of materials. The C6N2 and C6N4 perovskites exhibit a phase transition between 90 and 110 and 110 and 130 °C, in agreement with the DSC phase transition temperatures of 96 and 123 °C, respectively (see Figures S17–19). These results are consistent with the crystallographic data for the \((\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}\) series of materials, where because of the shorter organic linker the phase transitions (apparently from monoclinic to orthorhombic space groups) take place at temperatures lower than 25 °C for all structures \((n = 1−5)\) which at RT crystallize in orthorhombic space groups.\(^{53}\)

Indexing of the synchrotron PXRD data suggests that the materials undergo a space group change from monoclinic \((Cc\) and \(Pc\) for even and odd number of \(n\) respectively) at RT to orthorhombic \((Cc2m\) and \(C2cb\)) at high temperatures (see Figures S20–26), which is accompanied by a drastic increase in the unit cell volume (because of an increase in the size of the layer stacking axis). These high-resolution PXRD studies also shed light on the high-purity phase of the synthesized materials. It is evident that the current synthetic conditions afforded compounds C5N2–4 of pure phase (Figures S20–22), while C5N5 contains 1% C5N6 and 1% C5N4 phases, based on indexed PXRD patterns (Figure S23). Similarly, C6N2 was acquired in pure phase (see Figure S24), whereas C6N3 contains 1% C6N2 impurity (see Figure S25), and C6N4 contains 1% C6N3 impurity (see Figure S26).

Markedly, because of the high-quality data in the case of C5N4 it was possible to determine the crystal structure through the Rietveld refinement method at high temperature \((453 \text{ K})\) (see Figure 6). The structure crystallizes in the orthorhombic \(Cc2m\) space group (see Table S1) with a 3.2% slightly expanded unit cell volume as compared to the RT monoclinic structure because of thermal expansion. The \((\text{PbI}_2\text{Pb})_{11}\) in-plane equatorial tilting angles of the inorganic octahedra are 170.9(5)°, higher than the RT structure with values of 162.98(14)°, revealing a much less distorted structure, which is also verified by the perfect ordering of the planar pentylammonium cations among the layers (see Figure 6), as observed in the case of C5N1 orthorhombic phase structure.\(^{39}\) Furthermore, looking across the \(b\) axis in the orthorhombic C5N4 structure the adjacent octahedra in the same slab eclipse each other, while they are perfectly staggered to the octahedra of the adjacent slab (see Figure S27). However, in the case of the monoclinic C5N4 structure, adjacent octahedra in the same slab and among adjacent slabs are slightly displaced from the ideal staggered arrangement. This is in contrast to what was observed in the case of the monoclinic C5N1 structure, where the adjacent octahedra.
were in an eclipsed arrangement. The same type of displacement was observed for all monoclinic C5N2−5 compounds.

Thermogravimetric analysis (TGA) measurements shed light on the thermal stability of the new materials. Both families (PA)$_2$(MA)$_{n−1}$Pb$_n$I$_{3n+1}$ ($n = 1−5$) and (HA)$_2$(MA)$_{n−1}$Pb$_n$I$_{3n+1}$ ($n = 1−4$) are thermally stable up to 270 °C, just 25 °C below their 3D analogue MAPbI$_3$, where its first weight loss step appears at 295 °C. There are two distinct decomposition steps at ~270 and ~450 °C (Figures S28−36). The first weight loss corresponds to decomposition of the organic part of the structure and HI; the second step corresponds to evaporation of the inorganic part, PbI$_2$, above its melting temperature. The organic content of the 2D perovskites undergoes mass loss at the first decomposition step, which decreases gradually with increasing layer thickness, from 39% for the C5N1 to 32% for C5N5. Similarly, the inorganic step weight loss gradually increases from 57% to 60%, respectively.

**Optical Absorption and Photoluminescence.** Because the 2D hybrid perovskite structures are natural quantum wells with semiconducting slabs alternating with dielectric slabs, the band gap and the PL peak positions shift to lower energies with increasing layer thickness because of the quantum and dielectric confinement effects. The signature characteristic, deriving from these properties, is the presence of sharp excitonic peaks that gradually diminish with increasing number of layers. In the case of (PA)$_2$(MA)$_{n−1}$Pb$_n$I$_{3n+1}$ ($n = 1−5$) materials, the band gap ranges from 2.39 eV for the C5N1 to 1.76 eV for the C5N5 perovskites (based on the absorption edge), while for the HA analogs these values range from 2.34 to 1.85 eV for C6N1 to C6N4, respectively (Table 2 and Figure 7a and 7b). These results are similar for the $n = 2−4$ layers in both series, exhibiting only a small difference of 0.05 eV for the $n = 1$ materials, indicating that it is primarily the inorganic perovskite part of the structure that governs the optical properties of the materials. The main difference among them can be attributed to the distortion of the structure, represented by the Pb−I−Pb equatorial tilting angles. For example, C6N1 and C4N1 have almost the same energy band gaps of 2.34 and 2.35 eV, respectively, and tilting angles with

Table 2. Measured Band Gap Energy (eV) from the Absorption Spectra, Measured Valence Band Maxima (eV), and Corresponding PL Peak Positions (eV) for Both Families (PA)$_2$(MA)$_{n−1}$Pb$_n$I$_{3n+1}$ (C5N1−5) and (HA)$_2$(MA)$_{n−1}$Pb$_n$I$_{3n+1}$ (C6N1−4)$^a$

<table>
<thead>
<tr>
<th>no. of layers ($n$)</th>
<th>(PA)$<em>2$(MA)$</em>{n−1}$Pb$<em>n$I$</em>{3n+1}$</th>
<th>(HA)$<em>2$(MA)$</em>{n−1}$Pb$<em>n$I$</em>{3n+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>band gap (abs.edge) (eV)</td>
<td>band gap (excit.peak) (eV)</td>
</tr>
<tr>
<td>1</td>
<td>2.39</td>
<td>2.47</td>
</tr>
<tr>
<td>2</td>
<td>2.09</td>
<td>2.16</td>
</tr>
<tr>
<td>3</td>
<td>1.97</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>1.85</td>
<td>1.90</td>
</tr>
<tr>
<td>5</td>
<td>1.76</td>
<td>1.83</td>
</tr>
</tbody>
</table>

$^a$The band gap energy is calculated based on both the absorption edge and the exciton peak of the optical absorption spectra, while the PL energy is calculated by the PL peak position of the optical emission spectra.
values of 155.65(5)° and 155.08(2)°, whereas the CSN1 material with a more distorted structure (tilting angle 153.68(3)°) has a higher band gap of 2.39 eV, as it was also observed in the GAMAPbI$_4$ perovskite. The band gap values based on the excitonic peak positions are the same in all three RP families for BA$_2$-, PA$_3$-, and HA-based analogs ($n = 2$–$4$), verifying that indeed the nature of the insulating organic layer has a negligible effect on the optical properties of $n > 1$ layered perovskite structures but plays a more important role for the $n = 1$ structures.

The presence of stable excitons at RT leads to strong PL light emission for all of the title materials, ranging from 2.42 eV (512 nm) for CSN1 to 1.84 eV (674 nm) for CSN5 and 2.36 eV (525 nm) for C6N1 to 1.90 eV (652 nm) for C6N4 (Table 3 and Figure 7c and 7d). These values match closely the excitonic peak positions of the corresponding absorption spectra and match with the relative PL values of the BA-based materials (for $n > 1$). Time-resolved PL measurements shed light on the lifetime of the excitons, which lay in the range from 113 to 310 ps for the PA materials and from 113 to 303 ps for the HA analogs (Figures S37 and 38). These values are consistent with other multilayered 2D perovskites, such as the BA-based Ruddlesden–Popper materials, with values of around 200 ps, the AMP-based Dion–Jacobson with values in the range of 100–280 ps, and the PEA-based Ruddlesden–Popper with values of 158–189 ps.

Considering the importance of knowing the exact band energy structure of a semiconducting material that poses as a candidate in photovoltaic applications, we used ambient-pressure photoemission spectroscopy (APS) to gain insight into the electronic band alignment of the synthesized perovskite materials. The position of the valence band maximum (VBM) was determined through APS measurements, while the conduction band minimum (CBM) was determined by subtracting the corresponding band gap values (based on the absorption edge) from the measured VBM energies. The VBM values of the PA crystalline analogs range from 5.61 eV for CSN1 to 5.34 eV for CSN5, while for the HA materials these values vary from 5.51 eV for C6N1 to 5.31 eV for C6N4 (Figure 8). The error in these values is ±0.05 eV. The corresponding value for MAPbI$_3$ single crystals was also determined, as an internal method validation proof, and found to be 5.44 eV, matching to the widely accepted VBM value of 5.43–5.46 eV.

**Mechanical Properties.** When it comes to the implementation of a semiconductor material into real applications (photovoltaic, electronic, etc.), except for their environmental stability issues, another trait that must be taken into account is their mechanical properties. The inherent ability of a material to withstand mechanical stress and/or strain in plane and out-of-plane can determine to which extend and in which commercial applications these materials can be utilized.

Toward this end we evaluated the out-of-plane mechanical properties of C4N4, C5N4, and C6N4 2D perovskite single crystals through determination of Young’s modulus ($E$) and Hardness ($H$) by performing nanoindentation measurements. The Young’s modulus $E$ and hardness $H$ of C4N4 crystals ($E = 6.02$ ± $0.57$ GPa and $H = 0.76$ ± $0.09$ GPa) are higher than those of C4N3 ($E = 4.40$ ± $0.57$ GPa and $H = 0.43$ ± $0.07$ GPa) but lower than those of C4N5 ($E = 9.03$ ± $1.88$ GPa and $H = 1.06$ ± $0.29$ GPa) in accordance with our previous measurements (Figure 9). As an extra proof of validation of our method we synthesized large MAPbI$_3$ single crystals and determined the same out-of-plane mechanical properties. Apparently, the $E$ and $H$ values of the bulk MAPbI$_3$ crystals are $23.92$ ± $3.63$ GPa and $1.10$ ± $0.19$ GPa, respectively, which are much higher than the corresponding values of the 2D perovskites. Furthermore, these values are consistent with the reported literature values of $E = 23.9$ ± $1.3$ GPa, $E = 20$ ± $1.5$ GPa and $H = 1$ ± $0.1$ GPa, and $E = 23.68$ GPa.

The $E$ and $H$ values of C4N4 ($E = 4.88$ ± $0.59$ GPa and $H = 0.54$ ± $0.08$ GPa) and C6N4 ($E = 3.64$ ± $0.60$ GPa and $H = 0.35$ ± $0.05$ GPa) are higher than the corresponding values of C5N1 ($E = 2.65$ ± $0.43$ GPa and $H = 0.20$ ± $0.07$ GPa) and C6N1 ($E = 2.10$ ± $0.14$ GPa and $H = 0.21$ ± $0.02$ GPa), respectively, but lower than those of C4N4. It is clear that as the alkyl chain length of the spacer molecules increases from four carbon atoms (BA) to six atoms (HA), both $E$ and $H$ values decrease. This is reasonable as the amount of the softer organic part in the structure increases and the stiffer inorganic part decreases.

In the particular case of C6N4 perovskite, the $E$ value of 3.64 ± 0.60 GPa can be well compared to the Young’s modulus values of every day used polymers, such as Nylon-6 ($E = 3.15$ GPa), PS (polystyrene) $E = 3.72$ GPa, and PMMA (poly(methyl methacrylate)) $E = 3.83$ GPa. This increased structural flexibility and soft nature of the examined 2D

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**Figure 8.** Comparative band energy diagram of all synthesized perovskite crystals CSN1–5, C6N1–4, as well as MAPbI$_3$ for comparison purposes.
perovskite materials is beneficial as it could allow their utilization in flexible and wearable electronic devices, where their major competitors Si and GaAs with very high E values of 174.8 and 87 GPa, respectively, are much more stiff and unfavorable.

**Film Assembly.** The majority of the reported film fabrication protocols extensively utilize mixtures of precursor components (e.g., PbI₂, MAI, FAI, BAl, etc.) for film assembly in a glovebox. In the present study we used solutions made from single crystals to fabricate the corresponding films in air.

When casting 2D perovskite films a critical parameter that must be taken into account is the crystalline orientation of the perovskite on the substrate. As the structure of a 2D perovskite is anisotropic the inorganic layer will lay either parallel or perpendicular to the substrate. If parallel then charge transfer and collection is blocked leading to poor photovoltaic performance. Fortunately, the natural tendency of 2D perovskites with n > 2 is to deposit with the inorganic layers perpendicular to the substrate, leading to good performance, as we first reported. In the case where the inorganic layers are oriented vertical to the substrate the resulting PXRD pattern is dominated by 2 diffraction peaks corresponding to the (011) and (022) set of planes (monoclinic space groups). Considering, e.g., the C6N3 material, these peaks will occur at 14.1 ° 2θ and 28.4 ° 2θ (Cu Rad), respectively. Indeed, the calculated PXRD pattern assuming preferred orientation (March–Dollase) along these specific set of planes matches exactly the experimentally observed ones (Figure S39).

However, not all layered materials can be oriented along this specific direction, as the PXRD patterns of the low layered C5N2, C6N2, and C6N3 compounds using the one-step method (OS) (see SI) are consistent with randomly oriented polycrystalline samples (Figure S40a,e,f), similar to the C4N2 material.

The thin film crystallinity and vertical orientation of the inorganic layers can be enhanced by using the hot-casting (HC) method where the dissolved crystals’ solution is spin cast on a hot substrate. In the case of C6N3 and C5N5 compounds, this leads to a significantly improved preferred orientation of the layers and film crystallinity (Figure S41) as compared to the conventional one-step method (OS), where the solution is cast on the substrate at RT and then the substrate is postannealed at a specific temperature. The high crystallinity and vertical orientation of the 2D C5N3 and C6N3 films obtained from the HC method are further confirmed by synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements, where distinct Bragg spot features are observed predominantly in the out-of-plane (q_z) direction (see Figure 10e and 10f).

Contact angle measurements on the fabricated perovskite films MAPbI₃(A), C4N3(B), C5N3(C), and C6N3(D) and a drop of water. Contact angle increases with increasing length of the carbon chain of the organic spacer molecules in the 2D perovskites, resulting in increased hydrophobicity. Examined films were decomposed; however, this measurement offers a good indication of the effect of the organic spacer molecule on the hydrophobic properties of the materials. (Bottom) Synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) data of the HC-prepared C5N3 (E) and C6N3 (F) films on amorphous glass substrate.

**Figure 10.** (Top) Contact angles between the perovskite films MAPbI₃(A), C4N3(B), C5N3(C), and C6N3(D) and a drop of water. Contact angle increases with increasing length of the carbon chain of the organic spacer molecules in the 2D perovskites, resulting in increased hydrophobicity. Examined films were decomposed; however, this measurement offers a good indication of the effect of the organic spacer molecule on the hydrophobic properties of the materials. (Bottom) Synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) data of the HC-prepared C5N3(E) and C6N3(F) films on amorphous glass substrate.

heat and light stability of the corresponding films and devices. Here we provide a more comprehensive set of results under a variety of testing conditions for an extensive series of compounds. Examination of all three parameters (air, heat, and light stability) is very important as many of the test protocols for evaluation of solar cells aiming at commercialization, such as ISOS-D-3 (damp heat) and ISOS-L-3, require not only high levels of humidity (RH 50−85%) but also high temperatures (65−85 °C) and 1 sun illumination (AM 1.5G). Therefore, in order for our studies to be close to these stability parameters we fabricated thin films based on the new PA (C5N2−5) and HA (C6N2−4) perovskite materials and performed the following tests: (a) heat treatment at 100 °C in air, no encapsulation, RH 50%, (b) light stability under ambient light, no encapsulation, RH 50%, (c) light treatment under 1 sun in air, no encapsulation, RH 50%, (d) air stability in the dark, no encapsulation, RH 50−80%, (e) heat treatment at 100 °C in air, with encapsulation, and (f) light treatment under 1 sun in air, with encapsulation. Furthermore, two different film fabrication methods were used and evaluated, one step (OS) and hot casting (HC), as well as different film concentrations (0.35 M for HC only and 1 M for HC and OS), and for one material the air stability in the dark was tested for different substrates. For more details see the SI.
In order for the stability tests to be comparable among the different materials tested, the same synthetic conditions and solution concentrations (1M) were used for both film deposition methods. In particular, using the HC casting method another lower concentration was utilized (0.35 M) for comparison purposes. Profilometry measurements were performed in all cases to shed light on the film thickness, as this could be an important parameter for stability evaluation. The thickness of the films fabricated with the HC-0.35M method ranged between 185 and 250 nm, for the HC-1M method these values were between 780 and 900 nm, while for the OS-1M they ranged from 430 to 600 nm (Table S2).

**Effect of Deposition Method.** It is clear from the solution deposition behavior of the films that the HC leads to better growth orientation for most of the materials. For example, comparing C5N3−5 and C6N3 films from HC and OS methods (Figures S40−41) the diffraction peaks are narrower for HC and there are no low-angle diffraction peaks. Furthermore, judging from the full width at half-maximum (fwhm) of the (011) peak of the C5N4 OS and HC films (0.21° versus 0.16° respectively) there is a slight improvement in film crystallinity for the HC method.

Comparing the effect of the two methods on the heat stability of the examined films at 100 °C in air, under ambient light, at RH of 50%, the HC-1M-based compounds exhibit better stability, as the amount of formed PbI2, which is the major decomposition product of Pb-based perovskites in air (see PXRD patterns in Figures S32−60)90,91 is much less than in the corresponding OS-1M fabricated materials.

**Effect of Film Thickness.** Three different film thickness ranges (see above) have been tested for the heat stability tests of the examined materials at 100 °C in air, under ambient light, at RH of 50%. The film stability increases with film thickness for almost all examined materials, as judged by the decreasing amount of PbI2 (Figures S42−67).

**Effect of Film Substrate.** Perovskite C5N3 was cast using the HC method on 5 different substrates (amorphous glass, single-crystalline SiO2, PEDOT:PSS, FTO, and polycrystalline Si). The desired film orientation and very high crystallinity was observed in all cases, indicating that this fabrication method gives high-quality thin films on a variety of substrates, with different chemical substrate compositions (Figure S68).

Furthermore, for the C5N3 we tested the stability in air in the dark (RH 50−80%) cast on glass, single-crystalline SiO2, and polycrystalline Si (polycr.Si) (Figures 11a, 11c, and S69). The film fabricated on polycrystalline Si exhibited the best stability in air, as there was no formation of low-angle diffraction peaks with increasing time exposure. In contrast, in the case of glass-deposited film there was formation of the hydrate MAPbI3·H2O phase92,93 after 120 days. This implies that crystalline substrates may lead to films with higher crystallinity since the fwhm(011) values for the polycrystalline Si at 0.17° are lower than the 0.24° for the amorphous glass. They are also more oriented than those cast on amorphous substrates.

**Heat Stability in Air, No Encapsulation.** In this set of experiments the inherent thermal stability of films of MAPbI3, C4N4, C5N2−5, and C6N2−4 was examined after heating the corresponding films on a hot plate, at 100 °C, in air, under ambient light, with RH 50%, for 4 h. The effect of film thickness based on the different fabrication methods was discussed in the previous section. Therefore, in this section each deposition method (HC-1M, HC-0.35, and OS-1M) will be examined separately.

In the case of HC-1M-based films, visual examination suggests that the heat stability increases with increasing...
thickness of inorganic layer \((n)\). This is based on the emerging yellow color of the film indicative of formation of PbI_2, where it covers more area in the film of the lower \(n\) materials. However, PXRD measurements of the heat-treated films do not exhibit a clear trend, revealing that C5N4 and C5N5 exhibited the best thermal stability (Figures S47 and S48), although there is some formation of PbI_2 based on PXRD measurements yet there is no visual color change in the heat-treated films. Comparing C4N4, C5N4, and C6N4 films, it is clear based on PXRD that C5N4 and C6N4 exhibit much better thermal stability than C4N4, according to the trend C5N4 > C6N4 > C4N4 (Figures S47, S51, S43, and S44). By comparison, the 3D MAPbI_3 film shows a significant amount of PbI_2, revealing the inferior heat stability of the 3D analogue, although there is no color change on the heat-treated 3D film (Figure S42). A rather peculiar finding is the fact that although the C6N2 and C5N2 films had the same initial film crystallite orientation (inorganic slabs parallel to the substrate), the C6N2 decomposes almost completely to PbI_2 (Figure S49) while the C5N2 film seems intact with almost no color change after 4 h (Figure S45). The corresponding PXRD pattern of the latter (C5N2) shows that there is a change in the film crystal orientation upon annealing at 100 °C for 4 h, orienting the inorganic layers vertical to the substrate, as in the case of the higher \(n\) number films \((n \geq 3)\). This change in orientation (from the undesired parallel to the desired vertical) leads to an improved thermal stability as a result of the more efficient heat distribution through the film. The formation of a small amount of PbI_2 renders the stability of this \(n = 2\) film comparable to the higher layer materials, C6N4, C5N4, and C5N5. The fact that the film orientation can be adjusted by further annealing it for longer time may allow the use of C5N2 material as the upper absorbing layer in tandem devices \((E_g = 2.09 \text{ eV})\) or other electronic applications.

Examining the OS-1M-based films, an increase in the thermal stability with increasing number of inorganic layers was observed clearly only in the case of C6N2-, C6N3-, and C6N4-based films. Comparing the films of the \(n = 4\) based materials, the stability increases again in the order of C5N4 > C6N4 > C4N4, based on the amount of formed PbI_2 (Figures S52, S55, and S59). This means that C5N4 is the most stable, as it contained the least amount of PbI_2. Concerning the C5N2 behavior, the same result was also observed as in the case of the GC method. The orientation of the perovskite changed significantly (from the undesired parallel to the desired vertical) followed by improved thermal stability (Figure S53).

Regarding the HC-0.35M-based films, the effect of film thickness is clear, as these exhibit the lowest stability among the three used methods. Nonetheless, among C4N4, C5N4, and C6N4, C5N4 seems to exhibit the least thermal damage, as it is evident from PXRD measurements where the PbI_2 formation is limited (Figures S60, S63, and S67). Notably the C5N2 films decomposed in the same manner as the other films, without alteration in the film crystalline orientation as observed in both of the previous cases above. It is possible that because of the much thinner film for 0.35 M as compared to 1 M the system could not easily reorient and decompose rapidly.

**Light Stability in Air under Ambient Light, No Encapsulation.** In order to identify whether the 2D perovskite materials are sensitive even to ambient light, this set of experiments was designed to evaluate the air stability of compounds MAPbI_3, C4N4, C5N2–5, and C6N2–4 under continuous ambient light, with RH 50%, for up to 27 days. This examination involved the test of two different casting methods, HC-0.35M and OS-1M.

Regarding the HC-0.35M-based films, for the 3D MAPbI_3 analogue there is formation of a considerable amount of PbI_2 based on the recorded PXRD pattern (Figure S82); however, there is no change in film color. The stability increases as C5N4 > C4N4 > C6N4, the same trend as in the case of 1 sun light stability experiments (see below) (Figures S83, S87, and S90). C6N4 has the highest amount of PbI_2, while in C5N4 there was no detectable PbI_2 based on PXRD. This absence of PbI_2 signals the superior stability of C5N4 among all materials under the current examined conditions.

Because the OS-1M-based films are thicker than those from HC-0.35M solutions, they exhibit much better stability, up to 27 days in air, under continuous ambient light. For \(n = 4\), the stability increases in the following order C5N4 > C6N4 > C4N4. For that reason, C5N4 showed the best stability under these examined conditions.

**Light Stability in Air under 1 Sun Illumination, No Encapsulation.** The inherent light stability of compounds MAPbI_3, C4N4, C5N2–5, and C6N2–4 was also examined by exposing the films (HC-1M) under light, 1 sun solar simulator (AM 1.5G), with RH 50%, for 10 h. The 3D perovskite MAPbI_3 decomposed almost completely after 6 h based on PXRD measurements, where the diffraction pattern is dominated by formation of PbI_2 (Figure S72). The stability trend is C5N4 > C4N4 > C6N4. From the corresponding PXRD patterns, C6N4 tends to lose its optimum orientation, as there is the appearance of additional diffraction peaks from different diffraction planes, accompanied by formation of higher amounts of PbI_2 (Figure S81), whereas for C5N4 and C4N4 formation of PbI_2 is small (Figures 11b and S73). Additionally, in the case of C4N4 there is formation of the hydrated MAPbI_3·H_2O phase (Figures S73–74), which could be a result of the less hydrophobic nature of the film because of the shorter segment of the hydrophobic organic part. Comparing all materials, C5N5 exhibited superior light stability according to the PXRD patterns with no formation of PbI_2 and no loss of orientation (Figure S78).

Interestingly, although most of the diffraction patterns of the examined materials contain either a very small amount of PbI_2 or none as in the case of C6N3 (Figure S80), a large portion of the film has changed color, turning yellow, characteristic of PbI_2 and/or other solvated phases.

Notably, under illumination in air and no encapsulation the C5N2 and C6N2 behaved differently from the thicker layered materials. Not only C5N2 but also C6N2 films changed orientation upon light treatment (Figure S79), as observed for the C5N2 heat-treated sample, (see above). The orientation of the perovskites changed significantly, as the low-angle diffraction peaks \((<12^\circ \ 2\theta)\) disappear; however, C5N2 exhibited much better stability than C6N2, which based on PXRD analysis not only contains a higher amount of PbI_2 but also has lower crystallinity, as evidenced by the increase in the signal-to-noise ratio in the recorded pattern (Figure S79). To the best of our knowledge, this behavior of crystal reorientation in the film upon exposure to intense light or heat treatment is reported here for the first time in 2D perovskite-based films, and it may have serious implications on the device performance over extended periods of time.

**Air Stability in the Dark, No Encapsulation.** Taking into account the fact that perovskite compounds are air and light
sensitive. Based on the above results, we also performed air stability tests in the dark for MAPbI\textsubscript{3}, C4N4, C5N2–5, and C6N2–4 with RH ranging from 20% in the winter to 80% in the summer for more than 1 year. In this examination the OS-1M method was adopted for most of the materials, while in the case of C5N3 and C6N4, different substrates (amorphous glass, crystalline Si, and crystalline SiO\textsubscript{2}) were used.

In particular, except for MAPbI\textsubscript{3}, which decomposes rapidly in air, all other materials are stable in air in the dark for at least 120 days. There is no formation of PbI\textsubscript{2} nor change in film color; however, because of the high humidity levels in the summer time (≈80%) there was formation of a very small amount of the MAPbI\textsubscript{3} hydrate phase, marked by the blue asterisk in the corresponding PXRD patterns, Figures S99–104. Interestingly, the fabricated C5N3 films on crystalline Si (450 days in air), SiO\textsubscript{2} (150 days in air) (Figure S69), and C6N4 on SiO\textsubscript{2} (150 days in air) (Figure S70) exhibit much better air stability than on amorphous glass-deposited ones (120 days in air) (see Figures 11c and S104, respectively), as there is absence of the hydrate MAPbI\textsubscript{3} phase. The uniform surface of the crystalline substrates leads to better film crystallinity (see also Effect of Film Substrate), which results in enhanced air stability.

**Heat Stability in Air, with Encapsulation.** It has been established that if a perovskite film is protected from moisture and O\textsubscript{2} the stability is increased exponentially. This is usually achieved through encapsulation of the corresponding film using various methods, such as thermoplastic sealants and thermally or UV curable epoxies. For that reason we used a thermally curable thermoplastic sealant (Surlyn) to encapsulate the MAPbI\textsubscript{3}, C4N4, C5N4, C6N4, and C5N3-based films (OS-1M on amorphous glass and crystalline SiO\textsubscript{2}) and evaluate their thermal stability by heating the films on a hot plate, at 100 °C, in air, under ambient light, with RH 50%, for 12 days continuously. Details about the encapsulation process are given in the SI.

C4N4, C5N4, and C6N4 were chosen as benchmark materials considering the fact that C4N4 has demonstrated high PCE solar cells and the expectation that the longer-chain analogs may also exhibit high PCE, accomplished by improved environmental stability. Examining the heat-treated encapsulated films on amorphous glass, it is clear that yellow PbI\textsubscript{2} forms but only at the edges (Figures S105–108). This could be because of the insufficient protection near the edges leading to some degradation.

Comparing the materials that were cast on amorphous glass and encapsulated, MAPbI\textsubscript{3} was structurally intact after 12 days of continuous heat treatment, whereas in the 2D analogs after that time the stability follows the trend C5N4 > C4N4 > C6N4, based on the amount of detected PbI\textsubscript{2} from PXRD measurements of the uncovered films (removal of glass cover) after treatment. It is possible that this sealing method did not provide enough protection from the moisture, leading to some formation of PbI\textsubscript{2}. To test if this were the case, we fabricated new films based on C5N3 on crystalline SiO\textsubscript{2} and performed the same test inside a nitrogen-filled glovebox in the absence of moisture. These films were encapsulated with the same protocol as above. The films were then split into two groups. One group was placed on the hot plate continuously at 100 °C for 90 days, while the other group stayed for 40 days only 8 h per day at the same temperature (100 °C). When the encapsulation of the films was removed, PXRD measurements revealed that the film which stayed for 40 days 8 h per day was structurally intact, without traces of PbI\textsubscript{2}, or loss of crystallinity and orientation, while the film which was continuously exposed to 100 °C for 90 days exhibited a trace amount of PbI\textsubscript{2} and no visual color change (Figure 12). This again could be a result of the loss of the sealant protection ability rather than an intrinsic effect. The degradation of the sealant or loss of sealant protection is therefore minimized in the absence of moisture, providing absolute protection to the perovskite film. These results clearly indicate that if the perovskite is perfectly protected from moisture and O\textsubscript{2} then its stability is increased substantially (tested under extreme conditions, 90 days at 100 °C continuously, see Figure S109), rendering these materials suitable for real photovoltaic applications. The results also suggest that inherently these 2D perovskites are stable to light and any instability derives from interactions with external environmental factors (e.g., moisture, oxygen).

**Light Stability in Air, Under 1 Sun Illumination with Encapsulation.** In a similar manner, as in the previous test, the light stability of MAPbI\textsubscript{3}, C4N4, C5N4, and C6N4 was examined (OS-1M) by exposing the films to light, 1 sun solar simulator (AM 1.5G), with RH 50%, for 4 h per day for 15 days (60 h in total). Comparing all films, MAPbI\textsubscript{3} was the least stable; we observed severe damage, which lead to the formation of a huge amount of PbI\textsubscript{2} based on PXRD measurements (Figure S112). On the contrary, all 2D films exhibited far better light stability than MAPbI\textsubscript{3} in the following order C5N4 > C4N4 > C6N4, exactly the same order as in the unencapsulated experiment (light stability in air). C5N4 exhibited superior stability with zero formation of PbI\textsubscript{2} (Figure 11d). In the case of C4N4 and C6N4, however, there were some traces of yellow PbI\textsubscript{2} spots on the protected area of the film (inner area defined by the line of the sealant around the edges of the film) and on the unprotected edges of the films (Figures S110 and S111). Considering that the same stability trend is observed for films with and without encapsulation, we conclude that indeed C5N4 exhibits the best light stability among this family of 2D perovskite films and that proper

![Figure 12. Comparison of powder X-ray diffraction patterns (PXRD) for the as-made C5N3 synthesized with the OS method (1M) and 2 encapsulated films that were left at 100 °C inside a glovebox for 90 days continuously (blue pattern) and 8 h per day for 40 days (red pattern). The film that was left for 90 days continuously exhibits a trace amount of PbI\textsubscript{2} indicated by the green asterisk, while the one left for 8 h per day for 40 days is intact. This clearly verifies that if the films are sufficiently protected from moisture then their heat stability is very high.](image-url)
encapsulation of the films leads to much longer light stability, far superior to the 3D perovskites.

### CONCLUSIONS

The library of Ruddlesden–Popper-type 2D perovskite materials with general formula \((\text{cation})_2(\text{MA})_n\text{Pb}_x\text{I}_{3n+1}\) has been expanded by the use of pentylammonium (PA) and hexylammonium (HA) cations as organic spacer molecules \((n = 1–5)\). These materials have been synthesized using an optimized and universal methodology, which gave rise to uniform high-purity compounds, as verified by extensive characterization techniques. This represents a uniaxial expansion of the R–P family of materials along the layer stacking direction and goes two steps further from the butylamine \((\text{C}_4\text{N}_1)\) - and hexylamine \((\text{C}_6\text{N}_1)\) - based layered materials to pentylamine \((\text{C}_5\text{N}_1)\) - and hexylamine \((\text{C}_6\text{N}_1)\) - analogs. This generation of new perovskites allowed us to carry out a systematic and comparative study of comprehensive stability tests among its members. Utilization of high-resolution PXRD measurements shed light on the thermal stability, phase purity, and phase transitions of these higher layer 2D perovskites for the first time in the literature, revealing an increase in crystal symmetry with increasing temperature. The new materials have maintained the unique optical characteristics of the BA analogs, while at the same time they exhibit high air, heat, and light stability (especially for \(n = 4\)). Our extensive studies show the following: (a) the HC fabrication method leads to improved crystallinity and orientation in all of the higher layer materials and in all different examined substrates, revealing its general applicability, (b) the thickness of the film is critical, as the stability increases with increasing layer thickness, (c) crystalline substrates are essential for improved orientation and long-term air stability, (d) in terms of heat stability (100 °C) in air, for the same number of layers, the stability follows the trend \(\text{CSN}_4 > \text{C}_6\text{N}_4 > \text{C}_4\text{N}_4 > \text{MAPbI}_3\) regardless of the fabrication method and film thickness, (e) in terms of light stability (1 sun) in air the trend is \(\text{CSN}_4 > \text{C}_4\text{N}_4 > \text{C}_6\text{N}_4 > \text{MAPbI}_3\), regardless of the fabrication method and film thickness, (f) in terms of air stability under ambient light the trend is \(\text{CSN}_4 > \text{C}_4\text{N}_4 > \text{C}_6\text{N}_4 > \text{MAPbI}_3\) for the HC method and \(\text{CSN}_4 > \text{C}_6\text{N}_4 > \text{C}_4\text{N}_4\) for the OS method, (g) regarding the air stability in the dark all 2D materials are stable for more than 120 days when cast on amorphous glass substrates, while stability increases when cast on crystalline substrates, e.g., \(\text{CSN}_3\)-based film on crystalline silicon is stable in air for more than 1 year (450 days so far), \(\text{C}_6\text{N}_4\) and \(\text{CSN}_3\) films on crystalline SiO\(_2\) are stable for more than 150 days in air, and (h) for heat and light stability under encapsulation the stability decreases with the following order \(\text{CSN}_4 > \text{C}_4\text{N}_4 > \text{C}_6\text{N}_4\). One of the most important findings is that if the films are efficiently protected from O\(_2\) and moisture through a suitable sealant assembly the heat (e.g., 90 days continuously at 100 °C) and light stability increases drastically, validating that these materials are indeed inherently heat and light stable. This stability coupled with their soft and flexible nature, as verified by evaluating their mechanical properties, renders them suitable for wearable and flexible electronic devices, expanding their utilization beyond photovoltaic applications. Future studies should focus on the fabrication of optoelectronic devices based on this broad library of 2D perovskite halide materials as well as determination of the source of the superior environmental stability of pentylamine-based compounds, as compared to butylamine- and hexylamine-based analogs.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b01327.

Materials and methods, synthetic details, additional supplementary figures and tables about material characterization, SEM images, X-ray diffraction measurements, photoluminescence measurements, thermogravimetric analysis, profilometry measurements, and film stability studies (PDF)

Crystal data for compound \((\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) (CSN4) (CIF)

Crystal data for compound \((\text{CH}_3(\text{CH}_2)_5\text{NH}_3)_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) (CSN5) (CIF)

Crystal data for compound \((\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2(\text{MA})_2\text{Pb}_3\text{I}_{10}\) (C6N3) (CIF)

Crystal data for compound \((\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) (C6N4) (CIF)

Crystal data for compound \((\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2(\text{MA})_2\text{Pb}_3\text{I}_{10}\) (C5N3) (CIF)

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#### Notes

The authors declare no competing financial interest.

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