

# Enhanced Out-of-Plane Conductivity and Photovoltaic Performance in n = 1 Layered Perovskites through Organic Cation Design

James V. Passarelli,<sup>†, $\nabla$ </sup> Daniel J. Fairfield,<sup>‡, $\nabla$ </sup> Nicholas A. Sather,<sup>‡</sup> Mark P. Hendricks,<sup>⊥</sup> Hiroaki Sai,<sup>⊥</sup> Charlotte L. Stern,<sup>†,§</sup> and Samuel I. Stupp<sup>\*,†,‡,⊥,||,#</sup>

<sup>†</sup>Department of Chemistry, <sup>‡</sup>Department of Materials Science and Engineering, <sup>§</sup>Integrated Molecular Structure Education and Research Center, and <sup>||</sup>Department of Biomedical Engineering, Northwestern University, Evanston, Illinois 60208, United States <sup>⊥</sup>Simpson Querrey Institute for BioNanotechnology, and <sup>#</sup>Department of Medicine, Northwestern University, Chicago, Illinois 60611, United States

**S** Supporting Information

**ABSTRACT:** Layered perovskites with the formula  $(R-NH_3)_2PbI_4$ have excellent environmental stability but poor photovoltaic function due to the preferential orientation of the semiconducting layer parallel to the substrate and the typically insulating nature of the R- $NH_3^+$  cation. Here, we report a series of these n = 1 layered perovskites with the form (aromatic-O-linker-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> where the aromatic moiety is naphthalene, pyrene, or perylene and the linker is ethyl, propyl, or butyl. These materials achieve enhanced conductivity perpendicular to the inorganic layers due to better energy level matching between the inorganic layers and organic galleries. The enhanced conductivity and visible absorption of these materials led to a champion power conversion efficiency of 1.38%, which is the highest value reported for any n = 1 layered perovskite,



and it is an order of magnitude higher efficiency than any other n = 1 layered perovskite oriented with layers parallel to the substrate. These findings demonstrate the importance of leveraging the electronic character of the organic cation to improve optoelectronic properties and thus the photovoltaic performance of these chemically stable low n layered perovskites.

## INTRODUCTION

Two-dimensional organic-inorganic layered perovskites based on the lead halide framework have demonstrated many of the attractive optoelectronic properties and translational possibilities of their parent three-dimensional perovskites while achieving better stability.<sup>1-3</sup> The structure of these layered perovskites can be generally viewed as the periodic splitting of the three-dimensional structure along a particular crystallographic plane, most commonly along the (100) plane, to form a layered structure. Chemically, this is accomplished by substituting a bulky organic cation  $(R-NH_3^+)$  for the interstitial A-site cation according to the formula (R- $NH_3)_2Pb_nX_{3n+1}A_{n-1}$ .<sup>4,5</sup> In these structures, *n* corner-sharing PbX<sub>4</sub><sup>2-</sup> octahedra span the thickness of the inorganic layer where *n* is modulated by tuning the ratio of the small interstitial A site cation to the bulky organic cation (n = 1 shown in Figure 1A). These 2D semiconducting inorganic layers are separated by bulky organic cations, which are typically insulating and thus isolate the inorganic layers both physically and electronically.<sup>6–8</sup>

In the modern photovoltaic literature, the role of the organic cation has been primarily structural, and the optoelectronic properties of these materials have been designed through the compositional tuning of inorganic layers (varying X and n)<sup>9</sup> and processing conditions.<sup>10,11</sup> To date, these studies have achieved

remarkable results with a reported power conversion efficiency (PCE) of 12.5% for a layered perovskite where n = 4, R is butylammonium iodide, and A is methylammonium iodide.<sup>1</sup> In this example, the inorganic layers were oriented perpendicular to the bottom contact through a hot-casting technique to mitigate the negative impact of the insulating butyl groups on conductivity between the inorganic layers.<sup>1</sup> Even though the introduction of hydrophobic cations into these n > 1 layered perovskites has been shown to improve stability as compared to three-dimensional perovskites, most examples still utilize methylammonium iodide as the A-site cation, which is known to be intrinsically unstable under atmospheric conditions.<sup>9</sup> Furthermore, it is still unclear if the orientational control of the hot-casting technique is applicable to all cations in layered perovskites or for low *n* layered perovskites in general.

In this work, we study layered perovskites of the n = 1 variety where X = I. These n = 1 layered perovskites do not contain an A-site cation and are thus considerably more stable than the n >1 variety. These materials, however, present new challenges due to their wide bandgap and preferential orientation with inorganic layers parallel to the substrate. This leads to considerably lower PCE than devices with higher n active

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**Figure 1.** (a) n = 1 layered perovskites of the form  $(R-NH_3)_2PbI_4$  showing alternating organic and inorganic layers that align parallel to the substrate. (b) Modular molecular design of the ammonium iodide cation consisting of an aromatic core joined by an ether bond to an alkyl linker of variable length. (c) Energy levels of typical n = 1 layered perovskites (gray) with values specific to  $(butyl-NH_3)_2PbI_4$  as compared to the energy levels of the conjugated organic ammonium iodide salts of interest: perylene-*O*-ethyl-NH<sub>3</sub>I, pyrene-*O*-propyl-NH<sub>3</sub>I, and naphthalene-*O*-propyl-NH<sub>3</sub>I. HTL and ETL refer to hole and electron transport layers.

layers. The highest-performance n = 1 device with parallel orientation previously reported had a PCE of 0.12%.<sup>12</sup> Higher PCE has been achieved in one rare example where the inorganic layers prefer perpendicular orientation ( $\eta = 1.12\%$ )<sup>12</sup> and in another example where a conducting mesoporous scaffold likely resulted in an isotropic orientation and reduced charge transport distance in the active layer ( $\eta = 1.08\%$ ).<sup>13</sup> The favored parallel orientation of n = 1 layered perovskites requires conduction of excited-state carriers perpendicular to the inorganic layers and through typically insulating organic layers (out-of-plane conductivity) to reach the electrodes. If enhanced out-of-plane conductivity can be achieved in these materials, it would obviate the need to reorient the inorganic layers with

respect to the substrate surface in photovoltaic devices and result in a more generally applicable strategy for low-*n* layered perovskite devices.

Recent layered perovskite studies have utilized well-known organic moieties such as butylammonium,<sup>2</sup> benzylammonium,<sup>12</sup> and phenylethylammonium,<sup>3</sup> or other commercially available molecules where the desired optoelectronic properties were achieved through tuning of the inorganic lattice and postsynthetic modification.<sup>14–16</sup> However, preceding research of layered perovskites as photovoltaic materials, a number of investigators studied optoelectronic properties and functions with cations containing conjugated moieties such oligothiophene,<sup>17</sup> pyrene,<sup>18</sup> anthryl,<sup>19</sup> naphthalene,<sup>19</sup> and phenyl.<sup>20</sup> Much of this earlier work investigated the charge transfer of photoexcited carriers between the inorganic and organic layers and explored electroluminescent properties.<sup>17,18</sup> Their work showed the contribution that the organic chromophores can have on the optoelectronic properties and applications of these materials. They also demonstrated how the alignment of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the organic and inorganic layers can affect charge transfer between them in the hybrid.<sup>18</sup> Because this work predated interest in these materials as photovoltaic active layers, it primarily considered charge transfer from inorganic-to-organic layers or vice versa as a single event. However, charge transfer in a photovoltaic active layer requires many charge transfer events across many organic-inorganic interfaces through the thickness of the device. The predominant model for these materials has followed a multiquantum-well architecture where the electronic properties of the organic and inorganic layers have been considered separately.<sup>5,18,19</sup> Recent theoretical work has suggested that the orbitals of the organic moieties, particularly those that are aromatic, may contribute to the band structure of the inorganic.<sup>12,21</sup> Using inspiration from this work in organicinorganic layered perovskites as well as our own work on hybrid systems where the organic components serve both structural and electronic functions,<sup>22-24</sup> we report here on efforts to enhance photovoltaic performance in n = 1 layered perovskite through organic cation design.

In this work, we utilize the electronic and structural properties of custom-synthesized organic cations to achieve enhanced optoelectronic properties and device performance. We have synthesized organic cations containing various aromatic moieties and have explored how the electronic properties and structural arrangement of the cation within the organic galleries contribute to overcoming the chief limitation of n = 1 layered perovskites, which is their poor out-of-plane conductivity. Specifically, we have synthesized n = 1 layered perovskites with the formula (aromatic-O-linker-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> for which bulky cations are synthesized to contain the aromatic groups naphthalene, pyrene, or perylene and the linkers ethyl, propyl, or butyl conjugated through an ether bond (Figure 1A and B). We have investigated the impact of the HOMO and LUMO alignment of the organic cation and the inorganic layer as well as the structural arrangement of the organic cations within the organic layer on out-of-plane conductivity and optical properties of these layered perovskite materials. Guided by our findings, we fabricated photovoltaic devices and analyzed their performance.

	$(naphthalene-O-ethyl)_2Pbl_4$	(naphthalene-O-propyl) <sub>2</sub> Pbl <sub>4</sub>	(naphthalene-O-propyl- NH <sub>3</sub> )₂Pbl₄· (C₄H <sub>6</sub> O₂) <sub>0.5</sub>
Precursor Salt	ONH3+I-	ONH3'T	NH <sub>3</sub> 'I'
empirical formula	(C <sub>12</sub> H <sub>14</sub> ON) <sub>2</sub> PbI <sub>4</sub>	(C <sub>13</sub> H <sub>16</sub> ON) <sub>2</sub> PbI <sub>4</sub>	C <sub>2</sub> H <sub>3</sub> O(C <sub>13</sub> H <sub>16</sub> ON) <sub>2</sub> PbI <sub>4</sub>
formula weight (g/mol)	1091.27	1119.39	1162.37
cryst system	Monoclinic C	Monoclinic P	Triclinic
space group unit cell dimension:	Cc	$P_{2_1/c}$	ΡĪ
a, Å b, Å c, Å α, β, γ, deg	12.5228(17) 12.4668(17) 39.555(6) 90, 97.668(3), 90	23.0465(10) 8.8619(4) 8.2792(4) 90, 95.2834(19), 90	12.4181(3) 12.5652(4) 23.8888(7) 101.10, 104.07, 90.71
E <sub>S1</sub> (eV)	2.39 <sup>1</sup>	2.57 <sup>1</sup>	2.35 <sup>2</sup>
	(pyrene-O-ethyl) <sub>2</sub> Pbl <sub>4</sub>	(pyrene-O-propyl) <sub>2</sub> Pbl <sub>4</sub>	(pyrene-O-butyl) <sub>2</sub> Pbl <sub>4</sub>
Precursor Salt	0NH3+1	ONHgʻl	ONH3 <sup>+</sup> T
empirical formula	(C <sub>18</sub> H <sub>16</sub> ON) <sub>2</sub> PbI <sub>4</sub>	(C <sub>19</sub> H <sub>18</sub> ON) <sub>2</sub> PbI <sub>4</sub>	(C <sub>20</sub> H <sub>20</sub> ON) <sub>2</sub> PbI <sub>4</sub>
formula weight (g/mol)	1239.42	1267.48	1293.63
cryst system	Monoclinic C	Monoclinic C	Monoclinic C
space group	C <sub>c</sub>	C <sub>c</sub>	C <sub>2/c</sub>
unit cell dimension:			
a, A b Å	12.4263(3)	49.3795(13)	53.3048(16)
D, A C. Å	48 3623(3)	9 4484(2)	12 565(4)
α, β, γ, deg	90, 95.859(2), 90	90, 94.9469(13), 90	90, 90.318(2), 90
E <sub>S1</sub> (eV)	2.38 <sup>1</sup>	2.27 <sup>1</sup>	2.40 <sup>1</sup>
	(perylene-O-ethyl) <sub>2</sub> Pbl <sub>4</sub>		
Precursor Salt	NH3 <sup>+</sup> T		
empirical formula formula weight (g/mol)	(C₂₂H <sub>18</sub> ON)₂PbI₄ 1339.54		
cryst system	Monoclinic P		
space group	$P_{2_{1}/c}$		
a, Å b, Å	26.2873(9) 8.8638(3)		

#### Table 1. Crystal Data for n = 1 Layered Perovskites of the Form (Aromatic-O-linker-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>

(1) Energy of  $S_1$  exciton determined by optical absorption of thin films in transmission mode. (2) Energy of  $S_1$  exciton determined by optical reflectance spectroscopy on finely powdered crystals. Structures solved with direct methods using SHELXL and refined with least-squares minimization using the SHELXS refinement package. Additional crystallographic details are provided in the Supporting Information.

## RESULTS AND DISCUSSION

b, Å c, Å

α, β, γ, deg

E<sub>S1</sub> (eV)

**Synthesis and Characterization of Organic Salts.** We report here on a modular synthetic approach, which enabled the development of a homologous series of organic ammonium iodide salts that varied in both electronic character of the aromatic moiety and length of aliphatic linker. This approach

8.7113(3)

2.41<sup>1</sup>

90, 94.282(2), 90

facilitates the study of how the energy levels of the aromatic moieties and packing of the organic cations affect the optoelectronic properties of the resulting layered perovskites. Specifically, we synthesized six aromatic ammonium iodide salts with the general form aromatic-O-linker-NH<sub>3</sub>I where the aromatic moiety is naphthalene, pyrene, or perylene and the linker is ethyl, propyl, or butyl. The aromatic moieties were



## increasing $E_{S1}$ decreasing $d_{N-1}$

**Figure 2.** (a) Energy of the S<sub>1</sub> exciton versus average distance between the nitrogen cation and the peripheral iodides of the inorganic layers  $(d_{N-1})$  (left); (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> structure showing with dashed lines the four different N–I distances used to calculate  $d_{N-1}$  (right). Crystal structures showing intramolecular hydrogen bonding (if present) for (b) (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (c) (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. Note that the presence of an intramolecular hydrogen bond in the crystal structure acts to increase  $d_{N-1}$  and reduce  $E_{S1}$ .

chosen on the basis of reported HOMO and LUMO levels for the nonfunctionalized aromatic core in relation to the HOMO and LUMO levels reported for typical n = 1 lead iodide layered perovskites with aliphatic cations. To synthesize these ammonium iodide salts, hydroxyl-naphthalene, pyrene, or perylene were conjugated to either the protected bromoethyl, propyl, or butyl amine under basic conditions. Following purification, the protecting groups were cleaved and the resulting amine protonated with hydroiodic acid to form the final ammonium iodide salt (see the Supporting Information for synthetic details). Once synthesized, the HOMO and LUMO levels of the ammonium iodide salts were determined by ultraviolet photoelectron spectroscopy (UPS) and optical absorption experiments. These are plotted with respect to the HOMO and LUMO levels reported for the reported n = 1layered perovskite  $(CH_3(CH_2)_3NH_3)_2PbI_4^2$  in Figure 1C.

**Crystal Growth and Optical Properties.** The six aromatic cations with structure aromatic-O-linker-NH<sub>3</sub>I were successfully crystallized with lead(II) iodide into the desired (100) type n =1 layered perovskite. Single crystals were prepared through vapor diffusion of dichloromethane (DCM) into  $\gamma$ -butyrolactone (GBL) solutions of 2:1 molar ratio of organic ammonium iodide salt:lead(II) iodide.<sup>25</sup> We will refer to the resulting perovskites using an abbreviated formula of the general type  $(\text{aromatic-}O\text{-linker-}NH_2)_2PbI_4$ . Here, we report on seven n = 1layered perovskites including (naphthalene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (naphthalene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (naphthalene-O-propyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub>·(C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)<sub>0.5</sub>, (pyrene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (pyrene-O-butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, and (perylene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. The structures of these layered perovskites were determined using single-crystal X-ray diffraction. Crystallographic details are provided in Table 1

and Table S1. Note that naphthalene-*O*-propyl-NH<sub>3</sub>I can form two distinct layered perovskites. The first has the anticipated form and stoichiometry (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, and the second contains GBL within the lattice (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>·( $C_4H_6O_2$ )<sub>0.5</sub>. This was the only structure in this work that contained solvent molecules within the unit cell, and this structure could not be produced in thin film. All other layered perovskites were crystallized in thin film by spincasting and annealing the same stoichiometric ratios dissolved in a 1:1 volume ratio of dimethylformamide (DMF):dimethyl sulfoxide (DMSO). Grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to verify that the same crystallographic phase was obtained in thin film as observed in single crystal (Figures S1 and ST1).

Optical absorption spectroscopy was used to determine the energy of the  $S_1$  exciton peak  $(E_{S1})$  in thin film samples of each layered perovskite (Table 1 and Figure S2). Photoluminescence experiments were performed on thin film and single-crystal samples. The expected emission from the  $S_1$  exciton was observed only in the naphthalene containing layered perovskites (Figure S3). In all of the pyrene and perylene containing layered perovskites, both single-crystal and thin film samples showed no fluorescence signal above the autofluorescence background of the glass. This likely indicates enhanced nonradiative recombination processes in these materials that results in little or no observable fluorescence. These n = 1layered perovskites have characteristically large exciton binding energy in the range of 250-500 meV that results from the dielectric confinement of the 2D-inorganic layer.<sup>26</sup> The large binding energy is apparent in the absorption spectra with a pronounced lowest energy electronic transition, which is assigned to the S1 exciton followed by a broader absorption onset typically assigned to the bandgap absorption (Figure S4). The precise determination of the bandgap of these materials can be difficult to ascertain from the absorption spectra at room temperature. Thus, we used the  $E_{S1}$  transition as an indication of bandgap energy for these materials because this absorption has been shown to produce photocurrent and is thus important to photovoltaic performance.<sup>27</sup> A wide range of  $E_{S1}$  values (2.27-2.57 eV) have been observed for the layered perovskites investigated here. Increasing  $E_{S1}$  values are correlated with increasing distortion of the  $PbI_4^{2-}$  octahedra as compared to the ideal, lowest energy arrangement in which Pb-I-Pb bond angles along the central plane of the inorganic layer are 180° (Figure S5).<sup>28,29</sup> The role that the organic cation plays in dictating octahedral distortion and thus the optical properties of layered perovskites has been previously linked to the position of the positively charged ammonium cation with respect to the negatively charged inorganic lattice.<sup>28</sup> Our materials generally follow this previously defined model, except for (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, which has the highest  $E_{S1}$  despite having moderate penetration of the ammonium cation into the inorganic lattice (Figure S6). Recently, low octahedral distortion has been observed in an n = 1 layered perovskite containing tertiary ammonium groups.<sup>21</sup> In this structure, substitution on the ammonium group may increase the distance between the cationic nitrogen and the negatively charged inorganic lattice. In our materials, we have observed that  $E_{S1}$ values increase linearly with decreasing average cationic nitrogen to peripheral-iodide distance  $(d_{N-I})$  (Figure 2A). As  $d_{\rm N-I}$  decreases, the electrostatic interaction between the cationic nitrogen and negatively charged inorganic lattice increases, resulting in octahedral distortion and a higher  $E_{S1}$ .

The structural features of the organic cation must dictate  $d_{\rm N-I}$  and thus influence the resulting electrostatic interaction. Understanding and harnessing the structural properties of the organic cation to influence  $E_{\rm S1}$  and the bandgap of the layered perovskite will be crucial to the further development of these materials.

As mentioned previously, the  $E_{S1}$  values observed for the seven layered perovskites investigated here span 0.3 eV, a significant range for n = 1 layered perovskites. In most of these layered perovskites, the alkyl linker to the ammonium cation adopts an extended conformation within the organic galleries. However, this does not occur in (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> where we observe an intramolecular hydrogen bond between the ammonium cation and the ether linkage (Figure 2B). This intramolecular hydrogen bond hinders the extended conformation of the alkyl linker, resulting in just a 0.22 Å increase in the inorganic-to-inorganic layer spacing from (pyrene-Oethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> to (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. This is compared to a 1.77 Å spacing increase from (pyrene-Opropyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> to (pyrene-O-butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. The intramolecular hydrogen bond observed in (pyrene-O-propyl- $NH_3)_2PbI_4$  also appears to affect the  $d_{N-\mu}$  resulting in the longest observed  $d_{\rm N-I}$  and correspondingly the lowest  $E_{\rm S1}$  of 2.27 eV. Interestingly, when crystallized as a thin film, the same pyrene-O-propyl-NH<sub>3</sub>I molecule that creates (pyrene-O-propyl- $NH_3)_2PbI_4$  can form a different perovskite phase with a higher  $E_{S1}$  of 2.53 eV (Figure S7). This high  $E_{S1}$  phase has a larger inorganic-to-inorganic layer spacing than does (pyrene-Opropyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, suggesting that the alkyl linker in this phase adopts a more extended conformation. This conformation may decrease the  $d_{N-I}$  and thus raise  $E_{S1}$  as compared to (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, which contains an intramolecular hydrogen bond.

As noted previously, the naphthalene-O-propyl-NH<sub>3</sub>I molecule can form both (naphthalene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> and  $(naphthalene-O-propyl-NH_3)_2PbI_4 \cdot (C_4H_6O_2)_{0.5}$ . These perovskites demonstrate a structural trend similar to that of the two layered perovskites formed by the pyrene-O-propyl-NH<sub>3</sub>I molecule. The propyl linker in (naphthalene-O-propyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> adopts an extended conformation, and the material exhibits a high  $E_{S1}$  of 2.57 eV (Figure 2D). The second layered perovskite, (naphthalene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>·(C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)<sub>0.5</sub>, has a lower  $E_{S1}$  of 2.35 eV, and in two of the four molecules within the asymmetric unit of the crystal structure the propyl linker is disordered between two conformations (Figure 2C). In one, it adopts an extended conformation, but in the other it exhibits the same type of intramolecular hydrogen bond observed in (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. In both (naphthalene-O-propyl- $NH_3)_2PbI_4 \cdot (C_4H_6O_2)_{0.5}$  and (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, the propyl linker can form a six-membered intramolecular ring when the ammonium cation hydrogen bonds to the aromatic ether. When this intramolecular hydrogen bonding occurs, it reduces the optical bandgap by increasing  $d_{\rm N-I}$  within the structure. These results demonstrate the structural role that the organic cation can play in dictating the optical properties of the resultant perovskite and suggest new strategies to tune the optoelectronic properties by influencing  $d_{N-1}$  through intramolecular bonding and steric control.

**Out-of-Plane Conductivity.** To investigate how the electronic character of the organic cation affects out-of-plane conductivity, we measured the relative out-of-plane conductivity along the layered axis of single crystals for all of the layered perovskites reported in this work (except (naphthalene-*O*-

propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>·(C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)<sub>0.5</sub> due to the small sizes of crystals) as well as three aliphatic control crystals ((butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (hexyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, and (octyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>). These measurements were carried out using the devices described in Figure 3A, which used single crystals to eliminate the effects of grain boundaries on conductivity. These measurements were performed on multiple devices per crystal as well as multiple crystals of the same layered perovskite (Table S2). Representative current–voltage traces used for determining



**Figure 3.** (a) Schematic representation of the layered perovskite indicating the direction of conductivity measurements (left), and schematic of the device used to measure the out-of-plane conductivity and a colorized SEM of a single crystal drop-cast on a silicon wafer cleaved to reveal the cross section (right) (note the crystal is flat over its width (0.5 mm) and makes good contact with the substrate). (b) Conductivity of nine different n = 1 layered perovskites with either an aliphatic cation or a cation containing naphthalene, pyrene, or perylene (higher conductivity is observed for the pyrene and perylene samples, which possess better energy level alignment with the inorganic lattice). FTO refers to fluorine-doped tin oxide.

the out-of-plane conductivity of these crystals are provided in Figure S8. These traces are linear at low bias, which suggests ohmic contact between electrodes and the various crystals. The small series resistance introduced by the electrodes should be systematic and inherently incorporated into all of these measurements. Short circuits in this device geometry (direct contact between FTO and gold) generate many orders of magnitude higher current density than measurements through the crystals. Thus, we expect the contact resistance to be small as compared to that of the perovskite. The conductivity results show that the median conductivity spans close to 4 orders of magnitude, and the results are summarized in Figure 3B (under illumination) and Figure S9 in the dark (see Table S3 for numerical data). Generally, layered perovskites containing aliphatic cations were found to have the lowest conductivity, followed closely by the naphthalene-containing layered perovskites. Layered perovskites with pyrene and perylene cations were found to have substantially higher conductivity than those containing aliphatic moieties. This trend in conductivity mirrors the better alignment of energy levels between perylene and pyrene and the inorganic lattice (Figure 1C). This result indicates that the electronic character of the aromatic moieties within the organic galleries can be utilized to enhance out-ofplane conductivity in these materials.

In the design of these molecules, we included a variable linker length to study the effect of spacing between aromatic moieties and inorganic layers on out-of-plane conductivity. When comparing the three aliphatic controls and (naphthalene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, we found that their conductivities are on the same order of magnitude with a slight trend toward lower out-of-plane conductivity with increasing inorganic-to-inorganic layer spacings (Figure S10). Interestingly, a different trend was observed for layered perovskites containing pyrene. In this subset of layered perovskites, (pyrene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> and  $(pyrene-O-butyl-NH_3)_2PbI_4$  have effectively the same high conductivity of 4  $\times$  10<sup>-5</sup> S/m, while the conductivity of (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> is 2  $\times$  10<sup>-6</sup> S/m, which is considerably lower. This indicates that there is an additional structural aspect that is more significant than just the spacing between the inorganic layer and the aromatic core. We assume that n = 1 lead halide perovskites with the same aromatic moiety have similar carrier concentrations. Therefore, the large differences in conductivity should be due to mobility differences caused by the structural conformations of the aromatic cations that are not seen in the aliphatic controls. Examination of crystal structures for the three pyrenecontaining layered perovskites indicates that in the higher conductivity (pyrene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> and (pyrene-O-butyl- $NH_3)_2PbI_4$ , the organic cations exhibit edge-to-face type  $\pi$ stacking interactions when viewed down the layered axis across the van der Waals gap (Figure 4A and B). However, for the lower conductivity (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, an edge-toedge arrangement was observed in the crystal structure (Figure 4C).

Similar to the pyrene-containing layered perovskites, there is a significant difference in out-of-plane conductivity between the two naphthalene-containing layered perovskites. The lowest conductivity sample of all of the layered perovskites measured was (naphthalene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, which has a conductivity of  $1 \times 10^{-8}$  S/m, while (naphthalene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> has a significantly higher conductivity of  $3 \times 10^{-7}$  S/m. In the higher conductivity (naphthalene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, we observe edge-to-face type interactions (Figure 4d), whereas in the



**Figure 4.** Crystal structures of n = 1 layered perovskites ranked from left to right by highest out-of-plane conductivity to lowest where the structures in panels a and b have similar conductivity values: (a) (pyrene-*O*-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (b) (pyrene-*O*-butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (c) (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (d) (naphthalene-*O*-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, (d) (naphthalene-*O*-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, and (e) (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. The stacking of aromatic cores is highlighted with dashed lines within the organic galleries, and the square insets show a view down the layered axis from the perspective of an eclipsed aromatic core (viewing direction is denoted by the black arrow in the crystal structures).

lower conductivity (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, the structure reveals a staggered edge-to-edge stacking. This trend between the type of packing across the van der Waals gap and out-of-plane conductivity is the same as in the pyrene-containing layered perovskites. Last, (perylene-*O*-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> shows edge-to-edge type interactions (see Figure S11), although it has the highest recorded out-of-plane conductivity of all of the layered perovskites studied here. We attribute this to a better energy level alignment with the inorganic lattice as compared to materials containing the pyrene, naphthalene, or aliphatic cations.

The results described above suggest that, in addition to the electronic character of the aromatic moiety, their structural arrangement within the organic galleries plays a role in the observed out-of-plane conductivity. Specifically, edge-to-face interactions across the van der Waals gap yield enhanced conductivity as compared to edge-to-edge interactions. This is likely due to the comparatively better orbital overlap in the out-of-plane direction of the aromatic moieties, which is known to facilitate more efficient charge transport in organic single crystals.<sup>30–32</sup> This observation implies that future efforts to improve conductivity need to focus on how one controls the spatial arrangements of electronically active cations within the perovskite crystal. Finding strategies to further enhance orbital overlap possibly through face-to-face interactions may further improve out-of-plane conductivity.

**Device Fabrication and Photovoltaic Performance.** Given that poor out-of-plane conductivity is the chief limitation to the application of n = 1 layered perovskites in photovoltaic devices, the higher-conductivity layered perovskites in this work should exhibit enhanced photovoltaic device performance. Photovoltaic performance is of course also affected by optical absorption, crystallinity, and morphology of the active layer. Thus, we chose to focus on (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> for photovoltaic devices because it has the lowest energy S<sub>1</sub> exciton and therefore its absorption better matches the solar spectrum. Although this layered perovskite did not have the highest conductivity, it offered the best balance of properties for photovoltaic performance. As noted previously, thin films of (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> can crystallize into two different phases, and thus we selected annealing conditions (140 °C for 1 min) that resulted in predominant formation of (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> rather than the higher *E*<sub>S1</sub> phase.

Our best reproducible device architecture (Figure 5A) using  $(pyrene-O-propyl-NH_3)_2PbI_4$  achieved a power conversion efficiency (PCE) of  $1.14 \pm 0.11\%$  with a champion device performance of 1.38% (Figure 5B). These devices had a  $V_{oc}$  of  $1.02 \pm 0.03$  V,  $J_{sc}$  of  $2.43 \pm 0.14$  mA/cm<sup>2</sup>, and fill factor of 0.46 ± 0.02% across 27 devices (Figure S12). To our knowledge, this is the highest reported PCE for an n = 1 layered perovskite solar cell. This result is noteworthy given that grazing-incidence wide-angle X-ray scattering (GIWAXS) of our thin films shows a clear preferential orientation of the inorganic layers parallel to the substrate (Figure 5C), while the previously reported highest-efficiency n = 1 device had inorganic layers oriented perpendicular to the substrate.<sup>12</sup> Furthermore, our device is an order of magnitude higher efficiency than any other reported n= 1 layered perovskite with the inorganic layers oriented parallel to the substrate. We attribute this enhancement in performance at least partially to enhancements in out-of-plane



**Figure 5.** (a) Energy levels of the layers in the (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> layered perovskite solar cell. (b) I-V curve for the champion device with 1.38% efficiency (only forward sweep is shown for clarity, but the average includes forward and reverse curves where little hysteresis was observed (Figure S13)). (c) Grazing-incidence wide-angle X-ray scattering of (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> crystallized on a PEDOT:PSS-coated substrate. (d) AFM height and phase images for (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> crystallized on PEDOT:PSS. (e) Photograph showing the difference in appearance of three substrates dipped in water: the 3D perovskite with the formula (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub> and the n = 4 layered perovskite with the formula (butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> retains its original color.

conductivity in the crystalline material. Preliminary devices with  $(pyrene-O-propyl-NH_3)_2PbI_4$  showed that the PCE was significantly lower in low-crystallinity samples as compared to high-crystallinity samples, indicating that the photovoltaic performance is dependent on the crystalline phase rather than grain boundaries or defect states (Figure S14). External quantum efficiency results are shown in Figure S15. These results show no clear contribution of the pyrene absorption to the efficiency of the overall photovoltaic device. This is expected given the low absorption of pyrene within the visible spectrum and indicates that photovoltaic performance observed is due to the layered perovskite. With respect to charge transport layers, a low work function PEDOT:PSS formulation was used for better energy level alignment with the active layer, and no electron transport layer was added because the pyrene-O-propyl-NH<sub>3</sub>I molecule forms a native electron-transporting capping layer on the top surface of the active layer. A more detailed discussion of this capping layer, each device layer, device optimization, and UPS measurements is included in Figure S16 and ST 2.

The PCE of our devices using (pyrene-O-propyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> is at least 1 order of magnitude higher than control devices with (butyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> as the active layer using the same device architecture (Table S4). The (butyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> device required a charge transport layer to achieve photovoltaic function because butylammonium iodide does not form an electrontransporting capping layer on the surface of the active layer, unlike (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. Thus, to compare the two layered perovskites, we added a thin layer of 1-propoxypyrene on both (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> and (butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> active layers to mimic the native electron transport layer on the (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> active layer. These control devices demonstrate that 1-propoxypyrene functions as an electron transport for layered perovskite active layers, and that in this device architecture (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> as a photovoltaic active layer.

As previously discussed, GIWAXS was utilized to compare the orientation of the crystalline domains in these thin films. In both (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> and (butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (Figure S17), the films were found to be crystalline and oriented with the 2D layers parallel to the substrate. We analyzed the orientation of the thin films using Herman's orientation factor *S* to define orientational ordering.<sup>33</sup> An *S* value of 1 indicates perfect parallel orientation of domains, *S* = 0 indicates isotropic domains, and *S* = -0.5 indicates perfect perpendicular orientation of domains. By analyzing data along the azimuthal angle  $\chi$  from 0° to 90° within the *q* range of the (600) peak of (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, we found that S = 0.95, and within the *q* range of the (002) peak of (butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> we found that S = 0.97. This indicates strong alignment of the layered axis parallel to the substrate for both thin films (see ST 3 for derivation details). When analyzed by atomic force microscopy, thin films of (pyrene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> exhibit significant roughness and small grain sizes (Figure 5D). This is potentially caused by the low diffusivity of the bulky organic cation during the annealing process. The small grain size observed with this technique may explain some of the azimuthal peak broadening observed in GIWAXS.

Importantly, the active layer in these devices is chemically stable. Although the complete devices suffer from limited stability in atmospheric conditions due to reactions between the active layer and the cathode material, the active layer itself is exceptionally stable; it can withstand immersion in water for several minutes without any decomposition to lead(II) iodide (Figure S18). This property is unique when compared to the prototypical 3D perovskite (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub>, the n = 4 layered perovskite (butyl-NH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub>, and surprisingly the (butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (Figures SE, S19, and S20). This result demonstrates that the added hydrophobic bulk of large aromatic cations may act to enhance stability while maintaining higher conductivity as compared to aliphatic cations of similar size. This may result in additional stability and conductivity in higher-*n* layered perovskites.

## CONCLUSIONS

The out-of-plane conductivity in chemically stable n = 1 layered perovskites has been increased by several orders of magnitude using aromatic cations in the organic layers to better match their energy levels with those of inorganic layers. When used in photovoltaic devices, these layered perovskites yielded the highest reported power conversion efficiency (1.38%) for an n= 1 layered perovskite. We showed that intramolecular hydrogen bonding in the organic cations and supramolecular  $\pi$ -stacking interactions between them can result in narrower bandgaps and greater out-of-plane conductivity. Our results suggest there is great potential for functional improvement in chemically stable layered perovskites focusing on the design of the molecular and supramolecular structure of the organic layers.

### EXPERIMENTAL SECTION

Single-Crystal Preparation for Structure Evaluation and Conductivity Measurements. All single-crystal samples were prepared using vapor diffusion of dichloromethane into  $\gamma$ -butyrolactone (GBL) solutions containing a 2:1 molar ratio of organic ammonium iodide salt:lead(II) iodide. The concentration of GBL solution was critical to obtain high-quality samples for both singlecrystal X-ray diffraction and for electrical measurements (Table S5 and ST 4). In all cases, plate-like crystals, which ranged in color from yellow to red, appeared in ca. 24 h. These plate-like crystals form due to preferential crystal growth along the 2D inorganic galleries. To measure conductivity along the layered axis of these plate-like crystals, they were separated from their mother liquor and washed (details in ST 4) before being drop-cast on a freshly cleaned unpatterned FTO substrates (Solaronix, 15  $\Omega/\Box$ ). Small square gold pads of 113  $\mu$ m × 113  $\mu$ m × 50 nm were then thermally evaporated on top of the crystals through a TEM shadow mask (Electron Microscopy Sciences T200-Cu), and conductivity was measured on the single-crystal samples in a two-electrode geometry (Signatone probe station, Agilent 4155C semiconductor parameter analyzer). The conductivity was then measured through the thickness of the crystals and normalized by pad area and crystal thickness. Out-of-plane conductivity was measured both with the microscope lamp turned to full power (MLC-150C illuminator, 150 W EKE halogen lamp) and in the absence of any light. The conductivity was calculated using the linear region of the I-V curve (voltage sweep from -5 to 5 V) and parametrized based on individual device thicknesses. The thickness of each device was determined by optical profilometry (Zygo 3D Optical Profiler and Bruker Contour GT-K). The averages of multiple devices per crystal and across several crystals were taken to determine the out-of-plane conductivity of a given structure (Table S2).

Crystal Structure Determination. Single-crystal X-ray data were collected at room temperature on a Kappa Apex 3 diffractometer. For control crystals with previously reported structures, partial data sets were collected for unit cell determination (between 60 and 90 frames) to validate against the previously reported structures. For all other crystals, a complete data set was collected for structure solution and refinement. In all cases, the face-indexing tool in Apex 3 was utilized to verify the direction of the lavered axis for electrical measurements (Figure S21). Using Olex 2, crystal structures were solved using the ShelXS structure solution program using direct methods and refined using ShelXL refinement package using least-squares minimizations. The inorganic lattice was refined anisotropically without restraints. The organic cations were refined anisotropically with the exception of hydrogen atoms, which were placed in idealized positions. Additional restraints to the bond lengths and thermal ellipsoids for the organic cations were applied where necessary. Structural information for seven layered perovskites in this work is provided in Table 1 and Table S1. CCDC nos. 1840802-1840808 contain the supplementary crystallographic data for this Article.

Substrate Preparation. Glass and patterned ITO substrates (Thin Film Devices, 20  $\Omega/\Box$ ) were cleaned by sequential sonication in hexane, soapy water, milli-Q water, and a 1:1:1 mixture of isopropanol, acetone, and methanol. After drying, clean substrates were treated for 20 min in a UV-ozone cleaner (Bioforce Nanosciences). Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate in toluene (PEDOT:complex) (Ossila) was diluted to one-half of its original concentration with toluene and then filtered through a 0.2  $\mu$ m PTFE filter before spin-coating at 5000 rpm with a 5000 rpm/s ramp rate for 30 s. PEDOT:complex (Ossila) films were then annealed at 120 °C for 10 min in a nitrogen-filled glovebox. Poly(3,4ethylenedioxythiophene) polystyrenesulfonate in water (PEDOT:PSS) (Heraeus) was filtered through a 0.45  $\mu$ m nylon filter before spincoating at 5000 rpm with a 1000 rpm/s ramp rate for 60 s. PEDOT:PSS (Heraeus) films were then annealed at 150 °C for 20 min in a nitrogen-filled glovebox.

Thin Film Preparation. Thin film samples other than those intended for device active layers were prepared by spin-casting 2:1 molar ratios of organic ammonium iodide salt:lead(II) iodide (TCI Chemical) dissolved in 20-30 wt % in 50 vol % DMF/50 vol % DMSO onto freshly cleaned glass slides at 2000 rpm. With respect to solubility, we found that a combination of DMF and DMSO as a solvent mixture was very helpful in dissolving the poorly soluble bulky organic cations in our layered perovskite materials. From this solvent mixture, we spin-coated and annealed crystalline thin films of each of the layered perovskite materials. Each of the layered perovskites crystallized easily in thin films except for that containing the perylene derivative. These substrates were then annealed on a hot plate at 110 °C for 30 min. The resulting thin films were characterized by powder X-ray diffraction (PXRD) (Scintag XDS2000 using Cu K $\alpha$  radiation at 40 kV and 1-20 mA current), ultraviolet-visible absorption spectroscopy (PerkinElmer LAMBDA 1050), steady-state photoluminescence (Horiba Nanolog Fluorimeter), and grazing incidence wide-angle X-ray scattering (GIWAXS) (Beamline 8-ID-E Advanced Photon Source, Argonne National Laboratory). GIWAXS was performed with a beam energy of 10.92 keV and with a  $0.14^\circ$ incidence angle. The unit cell determined from single-crystal X-ray diffraction was compared by overlaying a predicted pattern<sup>34</sup> onto the GIWAXS patterns to verify the formation of the same phase in thin films and single crystals (Figure S1 and ST 1).

**Device Fabrication.** We designed the layers of our photovoltaic devices as shown in Figure 5A. The devices in this study were

fabricated in a nitrogen-filled glovebox. Pyrene-O-propyl-NH<sub>3</sub>I and lead iodide were dissolved at a 2:1 molar ratio in a 25 wt % solvent mixture of 50 vol % DMF/50 vol % DMSO and heated for 30 min at 65 °C. For optimized (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> devices, the active layer was spin-cast onto PEDOT:PSS-coated, patterned ITO substrates for 40 s at 4000 rpm with a ramp time of 7 s. The active layer was then annealed for 1 min at 140 °C. 50 nm silver contacts were thermally evaporated onto the substrates at a pressure of <10<sup>-6</sup> mbar using a shadow mask to define 4 mm<sup>2</sup> devices. More details about the device fabrication have been included in ST 2. Finally, devices were tested in air on a Newport solar simulator with a Keithley 2400 sourcemeter with a voltage ramp rate of 0.2 V/s.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03659.

X-ray crystallographic data for (naphthalene-O-ethyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> (CIF)

X-ray crystallographic data for (naphthalene-*O*-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (CIF)

X-ray crystallographic data for (naphthalene-*O*-propyl- $NH_3$ )<sub>2</sub>PbI<sub>4</sub> (C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)<sub>0.5</sub> (CIF)

X-ray crystallographic data for (pyrene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (CIF)

X-ray crystallographic data for (pyrene-O-propyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (CIF)

X-ray crystallographic data for (pyrene-O-butyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (CIF)

X-ray crystallographic data for (perylene-O-ethyl-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (CIF)

Synthetic details, characterization, experimental details, and additional figures as described in the text (PDF)

## AUTHOR INFORMATION

#### Corresponding Author

\*s-stupp@northwestern.edu

#### ORCID 0

James V. Passarelli: 0000-0001-7918-9392 Daniel J. Fairfield: 0000-0001-5880-2055 Mark P. Hendricks: 0000-0003-1295-9879 Hiroaki Sai: 0000-0002-4268-2148 Samuel I. Stupp: 0000-0002-5491-7442

#### Notes

The authors declare no competing financial interest.  $\nabla$  J.V.P. and D.J.F. contributed equally.

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