# Luminescent and Photoconductive Layered Lead Halide Perovskite Compounds Comprising Mixtures of Cesium and Guanidinium Cations

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**Supporting Information** 

**ABSTRACT:** Interest in hybrid organic—inorganic lead halide compounds with perovskite-like two-dimensional crystal structures is growing due to the unique electronic and optoelectronic properties of these compounds. Herein, we demonstrate the synthesis, thermal and optical properties, and calculations of the electronic band structures for one- and twolayer compounds comprising both cesium and guanidinium cations:  $Cs[C(NH_2)_3]PbI_4$  (I),  $Cs[C(NH_2)_3]PbBr_4$  (II), and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III). Compounds I and II exhibit intense photoluminescence at low temperatures, whereas compound III is emissive at room temperature. All of the obtained substances are stable in air and do not thermally decompose



until 300 °C. Since  $Cs^+$  and  $C(NH_2)_3^+$  are increasingly utilized in precursor solutions for depositing polycrystalline lead halide perovskite thin films for photovoltaics, exploring possible compounds within this compositional space is of high practical relevance to understanding the photophysics and atomistic chemical nature of such films.

# INTRODUCTION

Organic-inorganic layered lead halide compounds with perovskite-like structures are widely studied due to their fascinating electronic and optical properties and their rich structural chemistry.<sup>1-21</sup> Fundamental to the construction of perovskites is the formation of  $PbX_6$  octahedra (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and mixtures thereof) and their condensation into crystals that possess two- or three-dimensional (2D and 3D, respectively) corner sharing. Such extended 2D and 3D delocalization of electronic bands imparts semiconductive properties. Compounds with 3D arrangements and the generic formula of APbX<sub>3</sub> are formed when very small A-site cations are utilized  $(A^+ = Cs^+, CH_3NH_3^+, CH(NH_2)_2^+)^{.22-29}$  In contrast, larger A-site cations do not fit within the highly confined space between the octahedra. When a larger A-site organic cation is employed, the most likely outcome is the formation of 2D compounds, such as the compounds with the generic formula  $A_2PbX_4$  consisting of single layers of  $PbX_6$  octahedra sharing four of their corners, with the A cations in the interlayer space. Most of the known layered (2D) perovskite derivatives have mono- or diammonium cations, i.e., (RNH<sub>3</sub>)<sub>2</sub>MX<sub>4</sub> and (NH<sub>3</sub>RNH<sub>3</sub>)PbX<sub>4</sub>, respectively, where R is commonly an alkyl chain. The nonspherical geometry of RNH3<sup>+</sup> cations plays a significant role in the crystal symmetry of (RNH<sub>3</sub>)<sub>2</sub>MX<sub>4</sub> compounds, in addition to distortions and tilting of the PbX<sub>6</sub> octahedra, which are often caused by Jahn-Teller and/or

lone-pair effects.  $^{30-33}$  The orientation of the alkylammonium cations between the inorganic layers allows the ammonium groups  $(-\mathrm{NH}_3)$  to form hydrogen bonds with neighboring halogen ions.

These A<sub>2</sub>PbX<sub>4</sub> compounds can therefore be considered strongly quantum confined systems, i.e., quantum wells, wherein electron motion is limited to two dimensions. An interlayer organic entity acts as the potential wall. The variation in the carbon chain length in (RNH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> (from 4 to 14 carbon atoms) has a rather modest effect on the observed band gap energies. For example, the energies of the photoluminescence (PL) maxima are 2.35 eV for C4 and 2.4 eV for C10, confirming a highly localized quantum-well-like behavior.<sup>4,5,31</sup> Engineering the chemistry of these compounds at the interlayer space is of increasing interest,<sup>18</sup> with examples including intercalations of molecules such as hexane, dichlorobenzene, iodine, etc.<sup>34,35</sup> However, engineering the inorganic slab remains the principal approach to adjusting the absorption edges and PL maxima. For example, band gaps of 3.75, 3.17, and 2.55 eV are found for  $X^- = Cl^-$ ,  $Br^-$ ,  $I^-$ , respectively, in  $(C_{10}H_{21}NH_3)_2PbX_4$ .

Another strategy to tune the electronic structure is to increase the thickness of the lead halide slabs from a single layer to multiple layers, thereby tuning the band gap energies between

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the two limiting cases of 2D A<sub>2</sub>PbX<sub>4</sub> and 3D APbX<sub>3</sub>. Creating thicker slabs must involve at least two A-site cations, wherein the larger cation remains as an interlayer cation and the second cation fills in the smaller interslab cavities (which are of similar size as in the limiting case of APbX<sub>3</sub> compounds). Structurally, these compounds are analogues to the Ruddlesden-Popper phase, as in the case of  $(RNH_3)_2(CH_3NH_3)_{n-1}Pb_nX_{3n+1}$  (R =  $C_9H_{19}-$ , Ph-CH<sub>2</sub>CH<sub>2</sub>-; X<sup>-</sup> = Br<sup>-</sup>, I<sup>-</sup>).<sup>37</sup> Herein, a small CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> fills voids within the lead halide slabs, and the long alkyl chain ammonium ions are situated between the slabs, thus determining the interslab distance and defining the crystallographic orientation of the perovskite sheets. These phases can be seen as 2D slices of a 3D APbX<sub>3</sub> structure with various crystallographic orientations. For further crystallographic details of such compounds, we refer readers to recent review and research articles.7,

In  $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ , the band gap energies change from 2.43 to 1.91 eV as the thickness is adjusted from n = 1 to n = 4.5 Due to such tunability, these 2D systems are presently being intensively investigated for their optical properties and applications in light emission and in solar cells.<sup>1,4,31,40-42</sup> In particular, the archetypical 3D compound  $CH_3NH_3PbI_3$   $(n = \infty)$  had been reported recently as an outstanding photovoltaic material with power conversion efficien-cies repeatedly exceeding 20%.<sup>28,43–45</sup> However, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is known to undergo irreversible degradation due to the volatile nature of the decomposition products (methylamine, hydrogen iodide (HI), etc.), which is accelerated upon exposure to moisture, as in ambient air.<sup>46</sup> Higher chemical stability can be found within the family of  $(PEA)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$  (PEA =  $C_6H_5(CH_2)_2NH_3^+$ , wherein compounds with n = 1-3 have been synthesized and characterized in detail.<sup>47,48</sup> (PEA)<sub>2</sub>(CH<sub>3</sub>- $NH_3)_2Pb_3I_{10}$  (n = 3, band gap of 2.1 eV) exhibits higher chemical stability than  $CH_3NH_3PbI_3^{.48}$  The relevance of such structural motifs extends beyond lead-based halides; for example, in the tin iodide compounds  $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_nI_{3n+1}$ , for n > 3 metallic behavior is observed, while compounds with n < 3 are semiconductors.<sup>40</sup> However, tin-based compounds are highly prone to oxidation to Sn<sup>4+</sup>, limiting their practical utility.

In this work, we aimed to fully eliminate protonated ammonium salts, such as those in primary, secondary, or ternary alkylamines, from the construction of layered lead halide perovskites. To create monolayer A2PbX4-like compounds, we replaced the unstable CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> with a mixture of Cs<sup>+</sup> and guanidinium  $[C(NH_2)_3]^+$  ions. Guanidinium is an ideal alternative to the primary ammonium ions due to its thermodynamic stability, high basicity ( $pK_a = 13.6$ ), and strong hydrogen-bonding capabilities.<sup>49,50</sup> The high basicity of the guanidine molecule can be understood by considering a resonance stabilization of the guanidinium ion by 6-8 kcal/mol.<sup>51</sup> The guanidinium cation has been previously incorporated into a variety of perovskite-like salts with the formate (HCOO<sup>-</sup>) anion,  $[C(NH_2)_3][M^{II}(HCOO)_3]$ , where M is Mn, Co, Fe, Ni, Cu, Zn, or  $Cd.^{52,53}$  This suggests that guanidinium facilitates stable, highly symmetric structures. Although stable  $[C(NH_2)_3]_2$ - $Pb(Sn)I_4$  compounds have already been reported (with corrugated structure),<sup>54,55</sup> our interest was to test three further possibilities: (i) whether it is possible to mix such a stable organic cation with an inorganic cation at the interlayer and what structural effects accompany this combination, (ii) whether this mixture can also enable the formation of slabs thicker than one monolayer, and (iii) whether a noncorrugated structure can form. The small Cs ion is universally suited both for interlayer

locations and for filling the voids within the slab. In contrast, the guanidinium ion can be accommodated only in the interlayer space, despite being only slightly larger than  $CH_3NH_3^+$  and  $CH(NH_2)_2^{+.56}$ .

We succeeded in obtaining three layered perovskite compounds with n = 1, 2,  $Cs[C(NH_2)_3]PbI_4$  (I),  $Cs[C(NH_2)_3]$ -PbBr<sub>4</sub> (II), and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III), all of which contain (2D) slabs of corner-sharing octahedra and possess satisfactory thermal stability (up to 300 °C). Compounds I and II are luminescent upon moderate cooling, and compound III is emissive at room temperature. Photoresponsivities in the range of 1–10 mA W<sup>-1</sup> and with narrow-band characteristics were measured for compounds I and III, confirming their extended semiconductor nature.

#### METHODS

Chemicals, Reagents, and Synthesis Procedures. Lead(II) iodide (PbI<sub>2</sub>, 99%) and cesium bromide (CsBr, 99.9%) were purchased from Sigma-Aldrich. Lead(II) bromide (PbBr<sub>2</sub>, 98+%), hydrobromic acid (HBr, 48% water solution), and guanidinium carbonate (99+%) were purchased from Acros. Cesium iodide (CsI, 99.9%) and hydriodic acid (HI, 57%, stabilized with 1.5% hypophosphorous acid,  $H_3PO_2$ ) were received from ABCR. Diethyl ether (>99%) was dried over molecular sieves. All chemicals were used as received without further purification.

 $Cs[C(NH_2)_3]PbI_4$  (I),  $Cs[C(NH_2)_3]PbBr_4$  (II), and  $Cs_2$ [ $C(NH_2)_3]Pb_2Br_7$  (III) were synthesized from concentrated hydriodic and hydrobromic acids. The compounds were yellow (II, III) and red (I) microcrystalline powders (Figure S1 in the Supporting Information). A large excess ( $\geq$ 6-fold) of guanidinium ions was found to be necessary to obtain the desired compounds.

 $Cs[C(NH_2)_3]Pbl_4$  (I). CsI (1.55 mmol),  $[C(NH_2)_3]_2CO_3$  (6 mmol), and PbI<sub>2</sub> (1.55 mmol) were loaded into a 25 mL round- bottom flask, and 10 mL of HI acid (57% in water) was added carefully. Strong gas evolution was observed, and a red precipitate immediately formed. The precipitate was redissolved upon heating in a glycerol bath, yielding a clear yellow solution. Next, the flask was cooled under a cold water stream, causing the formation of a red crystalline precipitate of I. The solution remained undisturbed for another few hours to allow further precipitation. The precipitate was separated by vacuum filtration, washed with diethyl ether, and dried in a vacuum oven at 60 °C. A yield of 72% was estimated relative to Pb. To obtain larger crystals of I for photoconductivity measurements (0.5–2 mm<sup>3</sup>), the precursor solution was slowly evaporated at 60 °C instead of cooling.

 $Cs[C(NH_2)_3]PbBr_4$  (II). CsBr (2 mmol),  $[C(NH_2)_3]_2CO_3$  (6 mmol), and PbBr<sub>2</sub> (2 mmol) were loaded into a 25 mL round- bottom flask, and 10 mL of HBr (48%) acid was carefully added. Strong gas evolution was observed, and a yellow precipitate formed. Subsequent manipulations of the solution were identical with the procedure for compound I. A yield of 63% was estimated relative to Pb.

 $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III). CsBr (1 mmol),  $[C(NH_2)_3]_2CO_3$  (3 mmol), and PbBr<sub>2</sub> (2 mmol) were used for this synthesis. Upon addition of 12 mL of HBr (48%) acid, strong gas evolution was observed, and a yellow precipitate formed. Subsequent manipulations for the solution were identical with the procedure for compound I. A yield of 27% was estimated relative to Pb. To obtain larger crystals of III for photoconductivity measurements (0.5–2 mm<sup>3</sup>), the precursor solution was slowly evaporated at 60 °C.

 $(n-C_4H_9NH_3)_2PbI_4$  (IV). This compound was prepared according to Stoumpous et al.<sup>5</sup>

 $[C(\hat{NH}_2)_3]_2PbI_4$  (V). This compound was obtained as yellow platelets from a hot acidic solution using  $[C(NH_2)_3]_2CO_3$  (3 mmol), PbI<sub>2</sub> (2 mmol) and 7.5 mL of HI (57%). The crystals were separated by vacuum filtration, washed with diethyl ether and dried in a vacuum oven at 60 °C.

**CsPbBr<sub>3</sub> (VI).** This compound was crystallized from aqueous HBr using the corresponding bromides in stoichiometric quantities (0.15 M PbBr<sub>2</sub>, 0.15 M CsBr). Upon cooling to room temperature, orange



Figure 1. (a) Crystal structure of 2D  $Cs[C(NH_2)_3]PbI_4$  (I). (b) Hydrogen bonding between protons of guanidinium cations and iodine atoms of two 2D Pb–I layers. (c) Distorted Pb–I octahedral coordination.

crystals precipitated. Subsequent manipulations of the solution were identical with the procedure for compound I.

 $(n-C_4H_9NH_3)_2PbBr_4$  (VII). The synthesis of VII from hydrobromic acid was analogous to that of IV, using *n*-butylamine and PbO (in stoichiometric quantities, 0.5 M PbO, 1 M C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub>). Upon cooling to room temperature, colorless transparent plates crystallized. Subsequent manipulations of the solution were identical with the procedure for compound I.

**CsPb<sub>2</sub>Br<sub>5</sub> (VIII).** This compound was crystallized from stoichiometric quantities of the corresponding bromides in hydrobromic acid. Typically, CsBr (0.7 mmol) and PbBr<sub>2</sub> (1.4 mmol) were dissolved in 6 mL of hot HBr acid. Upon cooling to room temperature, colorless crystalline plates precipitated, followed by vacuum filtration, washing with diethyl ether, and drying in the vacuum oven at 60 °C.

 $[C(NH_2)_3]_2PbBr_4$  (IX). This compound was grown from a hot acid solution.  $[C(NH_2)_3]_2CO_3$  (4 mmol) and PbBr<sub>2</sub> (4 mmol) were loaded into a 25 mL round-bottom flask with 10 mL of HBr (48%) acid. The precipitate was redissolved upon heating in a glycerol bath, yielding a yellowish solution. Upon cooling to room temperature, colorless transparent crystals appeared within a few hours.

**CsPbl<sub>3</sub> (X).** This compound was crystallized in the form of orange needles from HI acid using the corresponding iodides in stoichiometric quantities as precursors (0.1 M PbI<sub>2</sub>, 0.1 M CsI).

**Characterization.** Powder X-ray diffraction (XRD) patterns were collected in the transmission mode (Debye–Scherrer geometry) using a STADI P diffractometer (STOE& Cie GmbH) equipped with a silicon strip MYTHEN 1K Detector (Fa. DECTRIS) with a curved Ge (111) monochromator (Cu K $\alpha_1$  = 1.54056 Å). Single-crystal XRD measurements were conducted using a Bruker Smart Platform diffractometer equipped with an Apex I CCD detector and a molybdenum (Mo K $\alpha$  = 0.71073 Å) sealed tube as an X-ray source. The crystals were tip-mounted on a micromount with paraffin oil. The data were processed using APEX3 (Bruker software), and the structure solution and refinement were performed with SHELXT and SHELXL programs embedded in the Olex2 software package. For twin indexing, the cell\_now algorithm (a part of the Bruker APEX2 software package) was used (see the crystallographic data section in the

Supporting Information). The obtained crystal structures of I, II, III and I' were deposited as CIF files into the CCDC database with the numbers 1552605 (I), 1552602 (III), 1552603 (II), and 1552604 (I'). UV–vis absorbance spectra of the microcrystalline powders were collected using a Jasco V670 spectrophotometer equipped with deuterium (190–350 nm) and halogen (330–2700 nm) lamps and an integrating sphere (ILN-725, working wavelength range of 220–2200 nm).

The absorbance spectra were estimated from reflectance and transmittance spectra collected from a thin layer of powder dispersed in an optically transparent Teflon grease and by diffuse reflectance transformed into absorbance using the Kubelka-Munk relation. The band gaps were estimated from the Kubelka–Munk function  $(F(R_{\infty}))$ , by subtracting excitonic peaks from the absorption edge. First, the excitonic transition was fitted with the Gaussian function. The residual spectrum was used to calculate  $[F(R_{\infty})\cdot h\nu]^2$  (where  $h\nu$  is the incident photon energy). Plotting  $[F(R_{\infty}) \cdot h\nu]^2$  versus energy  $(h\nu)$  gave a spectrum for estimation of band gaps. Although the fitting with a Gaussian function does not give an impeccable fit for the sub band gap region of the Urbach tail, this fit gives the possibility of estimating the band gap values. A better understanding of the spectral region at the Urbach tail can be attained by modeling according to the Elliott approach.<sup>57,58</sup> PL spectra were measured in a Joule-Thomson cryostat (MMR Technologies) operated in the temperature range of 78-300 K. PL emission was recorded with a heating rate of approximately 5 K/min. A 355 nm excitation source (a frequency-tripled, picosecond Nd:YAG laser, the Duetto model from Time-Bandwidth) and a CW diode laser with an excitation wavelength of 405 nm were used. Scattered laser emission was filtered out using dielectric long-pass filters with edges at 400 and 450 nm, respectively. The emission from the samples was collimated to an optical fiber and recorded at 1 K intervals with an SP-2300 spectrograph from Princeton Instruments coupled with a CCD array (LC100/M from Thorlabs). PL spectra were corrected to the spectral sensitivity of the setup using Planck irradiation from a calibrated halogen lamp. Time-resolved photoluminescence (TR-PL) measurements were performed using a time-correlated single photon counting (TCSPC) setup, equipped with a SPC-130-EM counting module

Table 1. Crystallograp	bhic Data for Selected Hybrid Lead H	lide Perovskites		
	$Cs[C(NH_2)_3]PbI_4$ (I)	$Cs[C(NH_2)_3]PbBr_4$ (II)	$Cs_2[C(NH_2)_3]Pb_2Br_7$ (III)	$Cs[C(NH_2)_3]PbI_4$ (250 K) (I')
formula wt	907.79	719.83	1299.66	907.79
temp (K)	300	300	300	250
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	Ртт	Imma	Сттт	Ртт
color	red	yellow	yellow	red
a (Å)	12.7426(13)	6.0613(6)	6.0029(12)	12.6947(12)
b (Å)	18.5776(19)	11.5868(12)	28.773(6)	18.6066(18)
c (Å)	12.2390(13)	17.4591(18)	11.598(2)	12.1767(12)
V (Å <sup>3</sup> )	2897.3(5)	1226.2(2)	2003.2(7)	2876.2(5)
Ζ	8	4	4	8
$ ho_{ m calcd}~({ m g/cm^3})$	4.162	3.899	4.309	4.193
$\mu \; (\mathrm{mm}^{-1})$	22.607	29.671	34.311	22.773
F(000)	3056.0	1240.0	2208.0	3056.0
cryst size (mm <sup>3</sup> )	$0.3 \times 0.07 \times 0.02$	$0.2 \times 0.08 \times 0.02$	$0.46 \times 0.08 \times 0.04$	$0.28 \times 0.1 \times 0.02$
radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Mo K $\alpha$ ( $\lambda = 0.71073$ )
2 <i>θ</i> range for data collection (deg)	3.876-63.122	4.218-62.904	3.512-62.718	3.884-60.052
index ranges	$-18 \le h \le 17, \\ -26 \le k \le 26, -17 \le l \le 17$	$-8 \le h \le 8,$ $-17 \le k \le 16, -25 \le l \le 24$	$-8 \le h \le 8, -41 \\ \le k \le 41, -16 \le l \le 16$	$-17 \le h \le 17$ , $-26 \le k \le 26, -17 \le l \le 17$
no. of rflns collected	33586	7142	11917	32295
no. of indep rflns	$4767 (R_{\rm int} = 0.0637, R_{\sigma} = 0.0432)$	1094 ( $R_{\rm int} = 0.0406, R_{\sigma} = 0.0295$ )	1814 ( $R_{\rm int} = 0.0473$ , $R_{\sigma} = 0.0370$ )	4385 ( $R_{\rm int} = 0.0600, R_{\sigma} = 0.0469$ )
no. of data/ restraints/params	4767/18/109	1094/0/40	1814/0/58	4385/18/87
goodness of fit on $F^2$	1.004	1.041	1.035	1.008
final R indexes $(I \ge 2\sigma (I))$	R1 = 0.0389, w $R2 = 0.0722$	RI = 0.0223, WR2 = 0.0519	RI = 0.0321, $wR2 = 0.0772$	R1 = 0.0352, w $R2 = 0.0806$
final R indexes (all data)	R1 = 0.0835, w $R2 = 0.0888$	Rl = 0.0261, WR2 = 0.0535	RI = 0.0407, w $R2 = 0.0823$	R1 = 0.0693, w $R2 = 0.0985$
largest diff peak/hole (e Å <sup>-3</sup> )	1.36/-1.55	0.84/-0.88	2.21/-1.52	2.44/-1.54

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Figure 2. (a, b) Crystal structures of 2D  $Cs[C(NH_2)_3]PbBr_4$  (II) and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III) perovskites. (c) Hydrogen-halogen bonds between protons of guanidinium cations and bromides of 2D layers of  $Cs_2[C(NH_2)_3]Pb_2Br_7$ . (d) Distortion of Pb-Br octahedral coordination in III and bromide split position in the crystal structure of  $Cs_2[C(NH_2)_3]Pb_2Br_7$ .

(Becker & Hickl GmbH) and an IDQ-ID-100-20-ULN avalanche photodiode (Quantique) for recording the decay traces. The emission was excited by a frequency-tripled ( $\lambda$  355 nm), picosecond Nd:YAG laser, the Duetto model from Time-Bandwidth, externally triggered at a 78 kHz repetition rate. PL emission from the samples passed through sets of long- and short-pass optical filters selecting the wavelength ranges 500–600 and 650–800 nm. Thermal analysis (thermogravimetry, TG, and differential thermal analysis, DTA) was performed using a NETZSCH STA 409 C/CD instrument in an alumina crucible under argon flow (40 mL/min) with a heating rate of 10 K/min.

**Photoconductivity.** Measurements were performed with illumination from a tungsten lamp dispersed by an Acton SP2150 (Roper Scientific) spectrograph/monochromator. The light was modulated by a mechanical chopper at a frequency of 13 Hz. The sample was gently pressed from two opposite sides by conductive rubber contacts in a custom-made holder and biased at 50 V through these contacts using a Keithley 236 SMU apparatus. The bias voltage was adjusted to obtain stable dark currents in the range of 1–10 nA. The signal, amplitude, and phase were measured across a series resistance by a Stanford Research 830 lock-in amplifier. The light intensity was controlled by a calibrated power detector (UM9B-BL, Gentec-EO). The current–voltage (I-V) characteristics were measured using a Keithley 236 SMU apparatus.

**Electronic Structure Calculations.** Two implementations of density functional theory (DFT) were employed. For the calculations of the band structure and density of states, we used the Dmol3 package within the Materials Studio suite.<sup>59,60</sup> For the real space representation of the bonding, we computed the electron localization function (ELF)<sup>61,62</sup> using Savin's implementation within the TB-LMTO-ASA code developed at MPI Stuttgart.<sup>63</sup> The ELF plots contain information on both ELF and electron density over a given plane

and were obtained using a code developed in-house. ELF values and electron density values are shown as the color of the pixels and the number of colored pixels, respectively, over a black background. Scalarrelativistic corrections were included in all calculations because they are expected to play an important role in the presence of heavy elements. The LMTO is an all-electron method, and in Dmol3 we chose to also include all electrons equally in the scalar-relativistic calculation, meaning that no pseudopotential was used. Within Dmol3, the tolerance for self-consistency was set to about  $10^{-6}$  Ha for the total energy, using the number of k points that results in a grid with separation smaller than 0.03  $Å^{-1}$  in reciprocal space. We employed the BOP (Becke one parameter) exchange-correlation functional, with which we have had in general better outcomes for the gaps in comparison with the commonly used PBE. For the LMTO calculations, we employed the Langreth-Mehl-Hu exchange-correlation functional. The self-consistency tolerance was set to  $10^{-5}$  Ry for the total energy and  $10^{-5}$  e for the atomic charges. Taking advantage of the speed of the LMTO code, the k space was sampled over 64-time denser grids than those used within Dmol3. The investigation of the effects on the band gaps due to spin-orbit coupling and nonlocal exchange interactions, which require the extensive use of semiempirical methods, should be the subject of future (and more computationally oriented) works.

# RESULTS AND DISCUSSION

**Crystal Structures of I–III.** The synthesized compounds were characterized by single-crystal XRD (Table 1 and Figures 1 and 2), powder XRD, thermal analysis (Figures 3), optical absorption, and PL spectroscopy (Figures 4 and 5). In addition, electronic structures were calculated by DFT methods.



Figure 3. X-ray diffraction powder patterns of (a)  $Cs[C(NH_2)_3]PbI_4$ , (b)  $Cs[C(NH_2)_3]PbBr_4$ , (c)  $Cs_2[C(NH_2)_3]Pb_2Br_7$ : comparison with simulated data from single-crystal analysis. Thermal stability analysis of I (d), II (e), and III (f).

The crystal structures were solved with direct methods; light elements (C, N) were located in the difference Fourier map, and hydrogen atoms were placed at calculated positions. Some of the crystals under investigation were twinned. Twin indexing and integration was performed with the Bruker Apex3 program software package. The compounds crystallize in the orthorhombic crystal system (centrosymmetric space groups Pnnm, Imma, and Cmmm for I-III, respectively; Table 1). The crystal structures of I and II feature single layers (n = 1) of PbX<sub>6</sub> octahedra, whereas compound III consists of a bilayer arrangement of the octahedra (Figures 1 and 2). To obtain the compound with n = 2, i.e.,  $Cs_2[C(NH_2)_3]Pb_2Br_7$ , the  $Cs:C(NH_2)_3:Pb_2Br_7$ molar ratio was adjusted to 1:6:2 during the synthesis. Further varying the molar ratios or thermal growth profiles during the crystallization did not yield compounds other than I-III. 2D layers were separated with a mixture of organic (guanidinium) and inorganic (cesium) cations in a 1:1 ratio, alternating in a periodic matter. As is typical for layered  $A_2BX_4$  systems (n = 1), neighboring layers are shifted by half of the octahedra with respect to each other (Figure 1a), maximizing the X-X distance for minimal electrostatic repulsion.<sup>64</sup> In all three compounds, the PbX<sub>6</sub> octahedra tilt, e.g., they deviate from the idealized Pb-X-Pb angle of 180°, to better accommodate the small  $Cs^+$  and large  $C(NH_2)_3^+$  cations. Guanidinium ions closely pack, with intermolecular  $d(C \cdots N)$  values in the range of 3-3.2 Å for all three compounds (Table S1 in the Supporting Information), and form hydrogen-halogen bonds with neighboring halogen ions (bromine or iodine, Figures 1b and 2c and Tables S5, S8, S11, S14, and S17 in the Supporting Information).  $Cs[C(NH_2)_3]PbI_4$  (I, Figure 1) exhibits somewhat higher structural disorder and stronger distortions in comparison to those of its bromide analogue. Both bridging iodides (along the *c* axis) of  $PbI_6$  octahedra can be represented as split into two positions (Figure 1c). All Pb-I bond lengths range from 3.101(2) to 3.226(1) Å. The average Pb–I distance is 3.168 Å, which is slightly longer than that in the cubic structure of CsPbI<sub>3</sub>, where d(Pb-I) = 3.1447 Å,<sup>65</sup> but smaller than that in the closely related (C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>, where d(Pb-I) = 3.184 Å was estimated.<sup>31</sup> Below 250 K, the crystals of I undergo extensive cracking into multiple new domains, prohibiting structural description of the newly formed phase(s). However, at exactly 250 K, crystal structure refinement is still possible, and certain conclusions can be drawn from the electron density map (this compound is denoted by I'). In particular, the disorder of the bridging iodides (*c* direction) is reduced, and they can be described by a single atomic position (Figure 1c). The Pb–I distances in I' are in the range of 3.145(1)-3.228(1) Å.

Compound II is a 2D compound with n = 1 (Figure 2a). Bridging bromides (Br3) (along the b direction) are disordered at two positions in the Pb-Br octahedra (Figure S2a in the Supporting Information). The distortion of the lead bromide octahedra could be described by Pb-Br3-Pb angles, which are equal to 157.488(3)°. Two apical and two bridging (along the a axis) bromides can be depicted as lying in the same plane with ideal 90° Br-Pb-Br' angles: d(Pb-Br1) = 3.030(1) Å and d(Pb-Br2) = 3.002(1) Å. Bridging bromide ions (along the *b* direction) are asymmetrically tilted at  $92.7^{\circ}$  with respect to that plane (Figure S2a) and have equal Pb-Br distances of 2.953(1) Å. Guanidinium ions form hydrogen bonds with halogen atoms of two different layers: d(H-Br) = 2.7445-2.869 Å (Figure S2b). The cesium ions occupy one type of position with a coordination number of 10 in the smaller voids between the Pb-Br octahedra.

Compound III represents a succession of  $Cs[C(NH_2)_3]$ -PbBr<sub>4</sub> with n = 2 (Figure 2b). The crystal structure of III consists of double 2D layers of Pb–Br octahedra with an average Pb–Br distance of 2.977 Å, which is slightly longer than that in cubic CsPbBr<sub>3</sub> (d(Pb-Br) = 2.937 Å).<sup>66</sup> Cesium occupies two types of positions in the structure: in the cavities within the double layers and in the space between the layers. The corresponding coordination numbers for the two positions are 8 and 10, respectively, with d(Cs-Br) = 3.775(1)-4.272(1) Å. Guanidinium is situated in the void created by the Pb–Br octahedra of the two 2D layers and forms hydrogen bonds with the neighboring Br ions of these two layers with d(H-Br)=2.804-2.847 Å, generating a 3D supramolecular network (Figure 2c). Bridging bromide ions (along the *c* direction) are disordered at a single position (Figure 2d).

Powder XRD patterns of the synthesized compounds were compared to a theoretical pattern (Figure 3a-c) for testing the overall purity of the substances. For compound I, no impurities were detected in the powder XRD pattern (Figure 3a). Compounds II and III often contain a few percent of each other as an impurity.

Thermogravimetric analysis was performed under inert conditions under an argon atmosphere (40 mL/min, ambient pressure), in alumina ( $Al_2O_3$ ) crucibles, at a heating rate of 10 K/min. Compounds I–III exhibit high thermal stabilities (Figure 3d–f). Decomposition starts at approximately 300 °C. Before decomposition, an endothermic process without a mass loss occurs for all three compounds: at 213 °C for II and III and at 283 °C for I, which is closer to the decomposition point. These endothermic processes indicate phase transitions, which could be melting or another structural transformation, which in the case of compound I is followed by the decomposition of the compound.

Absorption Spectra. Having established the crystal structures of compounds I-III, we examined their electronic structure using optical absorption spectroscopy (Figure 4a,b). In particular, we sought to compare the band gap energies with those for the known compositionally and/or structurally related compounds IV-X (Figure 4a-c and Figure S3 in the Supporting Information). These reference compounds were previously reported by other groups:  $IV_{,}^{5,11,31}V_{,}^{54}VI_{,}^{66,67}$ VII,<sup>1,68,69</sup> VIII,<sup>70</sup> IX,<sup>71</sup> and X.<sup>66</sup> In this work, compounds IV–X were grown from acidic solutions (see Methods). The purity of compounds I-X was assessed by comparing their powder XRD patterns with the simulated powder patterns generated using single-crystal data (see Figure 3a-c and Figures S4-S10 in the Supporting Information). Single-crystal data for some reference compounds were taken from ICSD cards 92045 (for V), 97851 (for VI), and 27979 (for X) as well as from ref 31 (for IV) and from ref 68 (for VII). Compounds VIII and IX, namely,  $CsPb_2Br_5$  and  $[C(NH_2)_3]_2PbBr_4$ , had not been structurally characterized prior to this study. Therefore, we determined their crystal structures by single-crystal XRD (for crystallographic details see Figure S3 and Table S2 in the Supporting Information and CCDC entries 1552606 and 1552601) and found good agreement with the powder patterns (Figures S8 and S9 in the Supporting Information). CsPb<sub>2</sub>Br<sub>5</sub> (VIII, Figure S3b) is a 2D compound with layers constructed of Pb-Br face-sharing distorted square antiprisms and cesium ions located in the interlayer space. This compound is often reported for Cs-Pb-Br systems, along with the 0D perovskite Cs4PbBr6 and 3D perovskite CsPbBr<sub>3</sub>.<sup>67,72,73</sup> Our single-crystal diffraction data for CsPb<sub>2</sub>Br<sub>5</sub> are consistent with a powder diffraction pattern reported in ref 70 and in PDF2 (#00-025-0211). [C(NH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>PbBr<sub>4</sub> (IX, Figure S3a) crystallizes in the triclinic  $P\overline{1}$  space group with a structural motif similar to that of  $[C(NH_2)_3]_2SnCl_4$ , as reported by Szafrański et al.<sup>74</sup>  $[C(NH_2)_3]_2$ PbBr<sub>4</sub> consists of 1D chains of corner-sharing [PbBr<sub>5</sub>] square pyramids, wherein the coordination



**Figure 4.** (a, b) Kubelka–Munk function  $F(R_{\infty}) = (1 - R_{\infty})^2 / R_{\infty} (R_{\infty} - \text{diffusive reflectance}) of I–IX. (c) Table of compounds and their band gaps determined from <math>[F(R_{\infty})hv]^2$  (after subtraction of the excitonic peak from the Kubelka–Munk function), where  $F(R_{\infty})$  is in Kubelka–Munk units and  $h\nu$  is the incident photon energy.

number of Pb(II) is 6, including the lone  $6s^2$  pair of electrons. The guanidinium cations are located between the inorganic chains and form hydrogen-halogen bonds, resulting in a 3D supramolecular structure. This structural analysis underlines the importance of Cs ions for building a stable 2D perovskite of compound II. Interestingly, the iodide compositional analogue  $[C(NH_2)_3]_2PbI_4$  (V) does form a 2D lattice, but unlike I, it is



Figure 5. (a–c) Normalized temperature-dependent PL spectra. The color bar (on the right) represents the intensity for all PL matrices. (d–f) Spectra at 77 K for  $Cs[C(NH_2)_3]PbI_4$  (I),  $Cs[C(NH_2)_3]PbBr_4(II)$ , and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III).

made of corrugated (zigzag) layers (see the structural comparison among I, V, and IV in Figure S11a-c in the Supporting Information).<sup>31,54</sup>

Figure 4a,b and Figure S12 in the Supporting Information present the normalized Kubelka–Munk (KM) functions,  $F(R_{\infty})$ , for all 10 compounds. This function is derived from the diffuse reflectance spectra of the powdered samples. This function is estimated as  $F(R_{\infty}) = \alpha/S = (1 - R_{\infty})^2/R_{\infty}$ , where  $\alpha$  is the absorption coefficient, S is the scattering coefficient, and  $R_{\infty}$  is the reflectance of an infinitely thick layer. Band gap energies were estimated by plotting  $[F(R_{\infty}) \cdot h\nu]^2$  (where  $F(R_{\infty})$  is in Kubelka–Munk units and  $h\nu$  is the incident photon energy) versus energy  $(h\nu)$ . The excitonic peaks were subtracted from the Kubelka–Munk function for the band gap determination (Figure S13 in the Supporting Information).<sup>57</sup> Conventional optical absorption spectra for all compounds I-X are presented in Figure S14 in the Supporting Information.

The most important comparison is between  $(n-C_4H_0NH_3)_2PbX_4$ (IV and VII) and  $Cs[C(NH_2)_3]PbX_4$  (I and II) because these compounds consist of flat sheets of  $PbX_6$  (unlike the corrugated sheets in V). The band gaps for the Cs guanidinium based compounds are smaller by 0.1-0.35 eV. This observation correlates well with the smaller interlayer ions reducing the average thickness of one layer (center to center distance) and, hence, also reducing the electronic isolation of the PbX<sub>6</sub> layers. For the case of iodides, the average thickness of one layer is 9.78 Å in I (13.8 Å in IV); correspondingly, the specific density of I is  $1.54 \text{ g cm}^{-3}$  greater than that of IV (4.162 g cm<sup>-3</sup> vs 2.702 g cm<sup>-3</sup>), whereas their molecular weights are similar (907.79 and 863.109 g mol<sup>-1</sup>, respectively), pointing to much smaller molar volumes obtained with smaller interlayer cations. Interestingly, despite its similar density, compound V shows a wider band gap of 2.63 eV (Figure 4c), arguably due to the corrugated 2D structure (Figure S11c in the Supporting Information). Another important factor is a distortion of the Pb-X octahedra. It can be described by a deviation of Pb-X-Pb angles from 180°. Moreover, in-plane (in the plane of propagation of inorganic layers) distortions were shown to

have a more significant influence on the band gap than the out-of-plane deviations.<sup>75,76</sup> When  $(n-C_4H_9NH_3)_2PbI_4$  and  $Cs[C(NH_2)_3]PbI_4$  are compared (Figure S15 in the Supporting Information), the difference in the band gaps is consistent with a degree of distortion of Pb–I octahedra. The in-plane deviation of the Pb–I–Pb angle from 180° for  $(n-C_4H_9NH_3)_2PbI_4$  is as significant as 24.36°, while for  $Cs[C(NH_2)_3]PbI_4$  the maximum angle of deviation is 18.43°.

The Kubelka–Munk absorption functions of 2D perovskites of variable slab thickness II and III point to a smaller band gap, as expected, for thicker Pb–Br slabs of III. In addition, the effect of the interlayer spacing is clearly seen in the approximately 0.35 eV wider gap of VII (flat 1D sheets) in comparison to that of II. Both II and III exhibit intermediate band gap values in comparison to those of compounds with higher and lower dimensionalities: i.e., CsPbBr<sub>3</sub> (VI, 3D) and  $[C(NH_2)_3]$ ,PbBr<sub>4</sub> (IX, 1D), respectively.

**Photoluminescence.** Optical emission spectra (Figure 5) were recorded in the range of 77–300 K for I–III. Only compound III exhibits a measurable PL intensity at room temperature (Figure 5c). All three compounds are brightly emissive to the naked eye under UV light at 77 K. For this temperature, Figure 5d–f present the luminescence spectra, while the entire temperature dependence is plotted as color maps in Figure 5a–c. The presence of minor emission peaks in Figure 5b,c suggests that compounds II and III contain small impurities of each other, as also concluded from the powder XRD patterns. For the PL spectrum of I, in addition to the main emission peak at 535 nm, a broader, low-intensity feature at 650–800 nm was detected.

In order to understand the origin of this feature, we performed time-resolved photoluminescence measurement at various temperatures (Figure S16 in the Supporting Information). It can be seen that while the emission at 535 nm decays very quickly, within 10 ns, the long-wavelength band relaxes much more slowly (sub $\mu$ s range) and the relaxation becomes even slower upon cooling to 200 K. These features of the spectrally broad and long-lived emission is consistent with the phenomenon of self-trapped excitons that was recently observed in 2D layered perovskites.<sup>35,76,77</sup> Often, the emission of self-trapped excitons accompanies narrow-band shorter-wavelength excitonic emission, such as in the present case.<sup>35,76</sup> Thus, we believe that we observed an excitonic emission at 535 nm and self-trapped excitons at 650–800 nm.

**Photoconductivity.** Semiconductive properties of the obtained compounds are manifested in the production of free charge carriers under light excitation and in the photoconductivity effects. The dark specific resistivity values are approximately  $3 \times 10^8$  and  $5 \times 10^9 \Omega$  cm for compounds I and III, respectively. The photoconductivity spectra (Figure 6) of two



Figure 6. Room-temperature photoconductivity of  $Cs[C(NH_2)_3]PbI_4$ (I) and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III) single crystals.

single crystals of compounds I and III exhibit similar features. First, a shoulder on the shorter wavelength side corresponds to band gap absorption. Second, sharp peaks appear at approximately 1 mA  $W^{-1}$  for Cs[C(NH<sub>2</sub>)<sub>3</sub>]PbI<sub>4</sub> (I) and 9 mA  $W^{-1}$  for  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III). Such photopeaks have been recently reported for APbX<sub>3</sub> perovskite single crystals<sup>72,78,79</sup> and can be explained by the thickness (depth)-dependent absorption and charge transport phenomena. Two competing effects determine the photocurrent in this case. First, the charges produced in the crystal volume are more effectively collected on the electrodes, while the charges produced on or close to the surface demonstrate decreased charge transport characteristics, likely due to the trapping of surface charges. When this trapping effect is combined with the absorption spectrum, a peak is expected at the onset of the absorption, not at the absorption peak. The wavelength of the peak, which is essentially equal to the band gap energy, is the wavelength at which sufficiently intense light propagates into the bulk region. At higher energies (shorter wavelengths), the higher absorption coefficient will limit the absorption to the near-surface regions. A third feature that differentiates compounds I and III form APbX<sub>3</sub> perovskite single crystals<sup>72,78,79</sup> is the long-wavelength photocurrent tail at energies well below the band gap; this tail is most pronounced for compound I. This region may be attributed to the photocurrent involving the midgap trap states. Interestingly, the charges produced in the SC volume (sharp peak and shoulder at longer wavelengths) are delayed in comparison to charges from the surface, corresponding to a decrease in the phase of the photoresponse (Figure S17 in the Supporting Information). This may be due to the moderate charge mobility in these compounds.

**Electronic Structure.** Compounds I–III have qualitatively similar electronic structures. We chose  $Cs[C(NH_2)_3]PbBr_4$  (II)

as an example for the following detailed discussion. The quantitative differences such as the band gaps and their relation to composition are addressed below. The density of states (DoS) per primitive cell is plotted in Figure 7. The solid black line



**Figure 7.** Electronic density of states (DoS) per primitive cell per eV in  $Cs[C(NH_2)_3]PbBr_4$  (II).

represents the sum of all valence states, and the contributions of selected species, i.e., the partial density of states (PDoS), are represented by colored areas.

The interaction of bromine with the other atoms is rather ionic, as can be inferred from the nearly 100% coverage (magenta areas) of the DoS in the regions where bromine contributes. The main contribution of lead to the occupied states originates from the electrons in the 6s orbitals at approximately 8 eV below the Fermi level, represented by the dashed gray area. The remaining valence electrons belong to guanidinium cations. The bonding, nonbonding, and antibonding combinations of the CN<sub>3</sub>  $\pi$  system are labeled in Figure 7. These states are not stabilized by the interaction with the protons and appear higher in energy. The nonbonding section has a negligible contribution from carbon (cyan area) as expected for the nearly ideal  $D_{3h}$  symmetry of guanidinium within this structure. The  $\pi$  contribution to the C–N bonds is also visible in the electron localization function (ELF, shown in Figure 8),<sup>61</sup> where the bc cut (left side) and the ac cut (right side) show different widths of the bonding attractor: i.e., the C-N bond cross section has an oval shape. The ELF also confirms the dominant ionic interaction between all Pb-Br and Cs-Br pairs, with the formation of nearly spherical closed shells. In the present case, the guanidinium-Br hydrogen bond is a proton bridge type of bond. Due to the deficit of one electron in the cation, the electron cloud is pulled by nitrogen and carbon toward the center, leaving the positive protons as an outer layer to interact with the bromine atoms. Accordingly, the very small contribution of hydrogen to the DoS (not highlighted in Figure 7) shows negligible mixing with bromine states. Note that the closed-shell-like ELF attractor of Br is distorted in a way that "avoids" the protons, which is typical for ionic interactions.

All three compounds feature guanidinium cation stacking in alternating orientations along a crystallographic axis, which suggests a stabilizing interaction between neighboring cations. We find that this stacking allows van der Waals interactions involving the easily polarizable  $\pi$  electron cloud of guanidinium cations. This conclusion is corroborated by the small contribution



**Figure 8.** ELF planar cut at x = 0 (left) and y = 0 (right), each covering  $2 \times 2$  unit cells of  $Cs[C(NH_2)_3]PbBr_4$ . Crystallographic sites are labeled with the name of the corresponding elements.

of the carbon states to the nonbonding peak just below -2.5 eV (see Figure 7). The latter can appear only if the  $D_{3h}$  symmetry is broken and the  $\pi$  electron cloud is polarized. At the same time, the  $\pi$ -bonding band appearing at -6.8 eV (see Figure 9) disperses along the W–R segment in reciprocal space. This band dispersion of approximately 0.7 eV is significant, especially



**Figure 9.** Electronic band structure of  $Cs[C(NH_2)_3]PbBr_4$  (II) from DFT calculations. The flatness of the majority of the occupied bands indicates the localized character of the states. Note the exceptional dispersion along the W–R segment of the  $\pi$ -bonding guanidinium states (in cyan at approximately –6.8 eV).

in comparison to the generally flat band structure of such systems. The alternate stacking allows the small energy cost for polarizing the shells to be overcompensated by the interaction between the induced dipoles, resulting in higher stability.

Compounds I–III are all semiconductors. DFT predicts that the highest occupied and lowest empty bands predominantly consist of halide p orbital and Pb p orbital contributions, respectively. The calculated band gaps are approximately 2.7 eV for Cs[C(NH<sub>2</sub>)<sub>3</sub>]PbBr<sub>4</sub>, 2.2 eV for Cs<sub>2</sub>[C(NH<sub>2</sub>)<sub>3</sub>]Pb<sub>2</sub>Br<sub>7</sub>, and 2.0 eV for Cs[C(NH<sub>2</sub>)<sub>3</sub>]PbI<sub>4</sub>. This trend is consistent with the measured absorption spectra (Figure 4) and can be understood in terms of basic quantum-mechanical principles. The band gap increases with the confinement, i.e., with the decreasing lead halide slab thickness (from n = 2 to n = 1) or on moving from heavier iodide to lighter bromide. Bromine is more electronegative than iodine, and therefore, the center of the valence and conduction bands should be closer in energy for the iodides (compound I), resulting in a smaller gap in this case.

#### CONCLUSIONS

In conclusion, we presented the synthesis and characterization of three layered lead halide perovskite compounds, containing a mixture of two stable interlayer cations in their structure (cesium and guanidinium): Cs[C(NH<sub>2</sub>)<sub>3</sub>]PbI<sub>4</sub> (I), Cs[C(NH<sub>2</sub>)<sub>3</sub>]PbBr<sub>4</sub> (II), and  $Cs_2[C(NH_2)_3]Pb_2Br_7$  (III). The two interlayer cations act synergistically to enable stable 2D perovskites through the van der Waals interactions between guanidinium cations and through hydrogen-halogen bonds between guanidinium cations and halide ions of different layers. Cs<sup>+</sup> ions fill the small voids within the Pb-Br layer in III, in addition to also occupying the interlayer space. All three compounds were shown to possess high thermal stability, up to above 300 °C. The compounds exhibit clear signatures of strong quantum confinement. Narrow-band photoconductive response was observed, indicating a balance between the optical absorption effects and the varying charge transport efficiency in the bulk and at the surface of the material.

These findings have strong relevance to perovskite thin-film photovoltaic research. In particular, recent studies have increasingly departed from the archetypical APbX<sub>3</sub>-like compound CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> to multicationic and multi-ionic formulations such as that in ref 80, wherein four A-site cations were used  $(CH_3NH_3^+, CH(NH_2)_2^+, Cs^+, Rb^+)$ . Moreover, adding guanidinium ions has been reported to improve solar cell characteristics.<sup>81,82</sup> Clearly, structural studies within this compositional space, as shown here for mixed-cation Cs–guanidinium systems, might unravel the complexities of such optoelectronic systems.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01204.

Photographs of compounds I and III under daylight and UV illumination (at 77 K), crystallographic data for I–III, VIII, and IX, absorption spectra for I–X, powder XRD for IV–X, comparison of crystal structures for I, IV, and V, excitonic peak subtraction from the Kubelka–Munk function of I, time-resolved PL spectra at various temperatures for I, and photoresponce for single crystals of I and III (PDF)

#### Accession Codes

CCDC 1552601–1552606 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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