2D Nanoplates and Scaled-Up Bulk Polycrystals of Ruddlesden–Popper Cs$_2$PbI$_2$Cl$_2$ for Optoelectronic Applications

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ABSTRACT: Two-dimensional (2D) layered Ruddlesden–Popper (RP) phases of halide perovskites offer exotic properties and interesting structure, which make them suitable candidates for solar photovoltaics, light emitting diodes (LEDs), and photodetector applications. Simple and scaled-up synthesis, chemical transformations, doping, and stability are the important steps toward the applications. Herein, all-inorganic RP phase of Cs$_5$Pb$_2$I$_8$Cl$_2$ was synthesized via a facile hot-injection method using benzoyl halides as halide sources. Different morphologies in the form of 2D nanoplates (NPLs) and small nanocrystals (NCs) were obtained by changing the concentration of capping agents (i.e., oleic acid and oleylamine) in solution. The excitonic absorption peak appeared for NPLs and NCs, which is the characteristic feature of 2D halide perovskites. Further, the scalable quantity (∼1 g) of bulk powder and micrometer-sized particles of Cs$_5$Pb$_2$I$_8$Cl$_2$ were synthesized via liquid assisted mechanochemical grinding and antisolvent method, respectively. We have performed post-synthetic chemical transformation to synthesize three-dimensional (3D) CsPbBr$_3$ disk-shaped particles and zero-dimensional (0D) Cs$_4$PbCl$_6$ NCs from the presynthesized RP Cs$_5$Pb$_2$I$_8$Cl$_2$ NCs in solution and studied their optical properties. Finally, doping of Mn$^{2+}$ was carried out in Cs$_5$Pb$_2$I$_8$Cl$_2$ NCs, which demonstrated a typical feature of Mn$^{2+}$ dopant emission along with host emission properties. Low-temperature (77 K) photoluminescence (PL) spectra reveal red-shifted and line-width broadening emission along with longer PL lifetime for both undoped and Mn-doped NCs compared to room temperature PL. Further, the temperature-dependent PL spectra and thermogravimetric analysis (TGA) revealed excellent thermal stability of Cs$_5$Pb$_2$I$_8$Cl$_2$. This work offers an insight for exploration of the synthesis process, post-synthetic chemical transformation, and dopant insertion in all-inorganic 2D RP perovskites, which is an important step forward for application. Demonstrations of various simple syntheses of both the nanophase and bulk phase, structural transformation, and detailed optical properties of doped and undoped RP perovskite halide nanostructures unfold innovative opportunities for applicability in optoelectronics such as in solar cell and photodetectors.

KEYWORDS: 2D halide perovskites, Ruddlesden–Popper phase, synthesis, post-synthetic transformation, Mn-doping, optical properties, thermal stability

INTRODUCTION

Metal halide perovskites are an important class of compounds due to their outstanding optoelectronic properties in terms of the narrow emission width, high quantum yields, tunable band gaps, faster carrier diffusion, smaller radiative lifetime, high carrier mobility, and low-cost solution processability.1–3 As a result, perovskite halides are favorable contenders for efficient light-emitting diodes, solar cells, photodetectors, etc.4–10 Among them, lead halide perovskites have drawn much attention due to their unique optical properties and defect-tolerant nature, which reflect in their astonishing optoelectronic properties.11 In spite of the impressive photovoltaic performance with ∼20% conversion efficiency,12–14 some disadvantages of hybrid metal halide perovskites (for example, CH$_3$NH$_3$PbI$_3$) have become pronounced with particular attention on the inadequate long-term stability.15 One possible solution for the aforementioned long-term stability issue was recommended in the form of layered perovskites, which is the 2D derivative of 3D perovskite family manifested by “slicing” the 3D framework into well-defined 2D slab.7,16 These lead halide-based 2D layered perovskites are becoming important prospects for LED applications due to their typical strongly bound excitons with high binding energies even at room temperature and rapid radiative decay rates.17,18 Currently, such low-dimensional perovskite halides like Ruddlesden–Popper (RP)19–21 and Dion–Jacobson (DJ)22 phases are...
regarded as the new frontier that justify remarkable recognition for solar photovoltaics and photodetectors.\(^{23}\)

Recently, in the hybrid RP perovskite halides, different large organic cations are introduced along the crystallographic planes at the A-site of \(\text{ABX}_n\) wedges.\(^{34}\) The represented chemical formula of RP phase is \(A_{n-1}A'B_nX_{n+1}\), where \(A'\) and \(A\) signify organic cations between diverse layers and small cations in the voids of the layers, respectively, whereas \(B\) and \(X\) denote the usual bivalent metal cations and halides, respectively. The number of metal halide monolayer sheets between the insulating \(A'\) organic layers is indicated as \(n\).\(^{20}\) Noteworthy advancement has been done in the field of 2D RP lead halide perovskites, mostly aimed at the hybrid organic–inorganic compounds with elongated organic chains.\(^{25,26}\) However, the presence of the long organic chains in the spacing layer of hybrid organic–inorganic RP phases provides negligible electronic coupling between inorganic perovskite layers.\(^{17,27}\) Thus, introducing an inorganic layer at the expense of a long organic spacing layer will offer reasonable interaction between the adjacent layers, which may result in superior chemical and thermal stability\(^{8,26}\) and exciting properties that are distinct from both the electronically uncoupled hybrid layered phases and 3D conventional perovskites.\(^{21}\) Fully inorganic RP halide perovskites are rarely explored so far.\(^{30-33}\) The generic formula to represent \(\text{Cs}^+\text{Pb}^+\text{X}^−\) based all-inorganic RP phase can be written as \(\text{Cs}^+\text{Pb}^+\text{X}^−_{n+1}\), in which the \(n\) layers of \(\text{CsPbX}_n\) unit are separated by an extra \(\text{CsX}\) layer.\(^{21}\) Recently, all-inorganic mixed halide RP phases have been reported,\(^{31-32}\) which possess the single-layer RP structure \((n = 1)\), as shown in Figure 1a. The synthetic strategies reported by Manna’s group used \(\text{PbX}_2\) as halide precursors,\(^{31}\) whereas Pradhan’s group used oleylamine–HCl and oleic acid–HCl as halide sources for the synthesis of all-inorganic RP \(\text{CsPbI}_2\text{Cl}_2.\(^{32}\)\) Previously, Manna and co-workers pointed out the limitation of using \(\text{PbX}_2\) during the synthesis of 3D \(\text{APbX}_3\), which was overcome by introducing benzoyl halides as halide precursors instead of \(\text{PbX}_2.\(^{34}\)\) The introduction of benzoyl halides offers a halide-rich environ-

\[\text{Cs}_2\text{PbI}_2\text{Cl}_2.\]
within a few seconds, and then the flask was kept at room temperature to cool slowly. Then, the Cs$_2$PbI$_2$Cl$_2$ nanostructures (∼10 mg) were collected by centrifuging at 8000 rpm for 10 min followed by washing with toluene (10 mL each time) 2−3 times. The details of the reaction scheme are shown in Scheme 1B.

Post-Synthetic Transformation of 2D Cs$_2$PbI$_2$Cl$_2$ to 3D CsPbBr$_3$. At first, precursor solution of PbBr$_2$ was prepared by taking 183.5 mg (0.5 mmol) of PbBr$_2$ and 5 mL of ODE in a three-necked round-bottom flask in the Schlenk line. An amount of 0.5 mL of each OA and OAm was added at N$_2$ atmosphere, and the temperature was increased to 120 °C and kept until all PbBr$_2$ dissolved. Then, the temperature of the precursor solution was decreased to room temperature and toluene dispersed Cs$_2$PbI$_2$Cl$_2$ was injected swiftly. Within 1 min greenish yellow colored CsPbBr$_3$ NCs started to form, and then the solution was centrifuged at 9000 rpm for 10 min. The synthesized CsPbBr$_3$ NCs were washed 2−3 times by toluene.

Post-Synthetic Transformation of 2D Cs$_2$PbI$_2$Cl$_2$ to 0D Cs$_4$PbCl$_6$. Similarly, precursor solution of MnCl$_2$ was prepared by taking 63 mg (0.5 mmol) of MnCl$_2$ and 5 mL of ODE in a three-necked round-bottom flask in the Schlenk line. 1 mL of OA and 1 mL of OAm were added and dried under vacuum for 2 h at 130 °C along with magnetic stirring. Subsequently, the temperature was increased to 160 °C under N$_2$ atmosphere and 1:1 mixture of benzoic chloride and benzoic iodide was injected swiftly and the flask was allowed to cool to room temperature slowly. Then the as-synthesized Mn doped Cs$_2$PbI$_2$Cl$_2$ nanocubes were collected by centrifuging at 8000 rpm for 10 min and washing with toluene 2−3 times.

Synthesis of Cs$_2$PbI$_2$Cl$_2$ by Liquid Assisted Grinding (LAG). In a typical synthesis, 113.6 mg (0.5 mmol) of CsI and 117.38 mg (0.25 mmol) of PbCl$_2$ were taken in a stoichiometry ratio in a mortar pestle, and a few drops of organic solvent (EtOH/DMF) were added in two different reactions. The mixtures were ground mechanically for about 2 h in a N$_2$ filled glovebag. After 2 h, the pure phase of Cs$_2$PbI$_2$Cl$_2$ was formed when DMF solvent was used. The details of the liquid assisted grinding (LAG) are shown in Scheme 1D.

Synthesis of Cs$_2$PbI$_2$Cl$_2$ by Antisolvent Reprecipitation Method. For the synthesis of colloidal Cs$_2$PbI$_2$Cl$_2$, CsI and PbCl$_2$ were taken as a 2:1 molar ratio and dissolved in 2:1 volume ratio of DMSO and DMF to form a precursor solution. Typically, 52 mg (0.2 mmol) of CsI and 27.8 mg (0.1 mmol) of PbCl$_2$ were dissolved in a
mixture of 2 mL of DMSO and 1 mL of DMF to form total 3 mL of precursor solution. Then 200 μL of precursor solution was injected into 5 mL of toluene under vigorous stirring of a few minutes. Then the solution was centrifuged at 8000 rpm for 10 min and washed with toluene 2–3 times. The details of the antisolvent reaction scheme are shown in Scheme 1E.

**Powder X-ray Diffraction (PXRD).** The PXRD measurement was carried out by a Bruker D8 diffractometer with Cu Kα (λ = 1.5406 Å) radiation.

**Transmission Electron Microscopy (TEM).** The TEM measurement was performed using a JEOL (JEM3010) TEM instrument (300 kV accelerating voltage) fitted with a Gatan CCD camera.

**Field Emission Scanning Electron Microscopy (FESEM).** FESEM images were acquired by a Tescan-Mira 3 LMH.

**Electronic Spectroscopy.** Electronic absorption spectroscopy of NPLs and NCs was performed in solution phase by PerkinElmer, Lambda-900 UV/vis/near-IR spectrometer. Diffuse reflectance measurements were carried out in the range of 250–800 nm to estimate the optical band gap in the solid state sample. The emission spectra were recorded on a PerkinElmer LS 55 luminescence spectrometer in solid state and solution phase at room temperature. Low-temperature PL measurements were performed using an Edinburgh FLS1000 spectrophotometer and excited with EPLED-340 (wavelength 340 nm ±10 nm) at 77 K using a vacuum liquid-nitrogen cryostat.

**Fluorescence Lifetime and Quantum Yield Measurements.** A Horiba Delta Flex time-correlated single-photon-counting (TCSPC) instrument was employed to acquire time-resolved decay plots in which a 373 nm nano-LED was used as the light source with 1 MHz of pulse repetition rate. Ludox AS40 colloidal silica (Sigma-Aldrich) was utilized as scatterer to accumulate the instrument response function (IRF). The instrumental full-width at half-maximum (fwhm) together with detector response was found to be 0.2 ns for the 373 nm LED light source. The collection of the excited state decay of synthesized samples was performed by choosing a fixed emission wavelength. For 590 nm of emission wavelength, a 355 nm spectra LED light source was used. The decay was fitted by using IBH software (DAS6). The average lifetime (τ_{ave}) values of NCs were calculated by following equations: τ_{ave} = \sum A_i \tau_i^2/(A_i \tau_i) where, A_i and \tau_i are the fraction of the ith component and decay time, respectively. The absolute photoluminescence quantum yield (PLQY) values were measured using an Edinburgh FLS1000 spectrophotometer with a

Figure 2. TEM images of (a, b) Cs2PbI2Cl2 NPLs and (d, e) Cs2PbI2Cl2 NCs. HRTEM images and SAED patterns (insets) of (c) Cs2PbI2Cl2 NPLs and (f) Cs2PbI2Cl2 NCs.
calibrated integrating sphere (λex = 380 nm). Samples were prepared in glass substrates by drop casting the solution and subsequently, inserted in the sample holder for PLEQY measurement.

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis was carried out using a 2 STAR TGA instrument, in which the samples were heated in N2 atmosphere (40 mL min−1) at a rate of 5 °C min−1 in the temperature range of 50–800 °C.

**Elemental Analysis.** A PerkinElmer Optima 7000DV inductively coupled plasma atomic emission spectroscopy (ICP-AES) instrument was employed to measure the amount of Pb and Mn present in Cs2Pb0.5Mn0.5I3Cl nanocrystals. The standard solutions were prepared with ICP standards of Pb and Mn (1000 mg L−1, Sigma-Aldrich). Samples were dissolved in concentrated nitric acid to acquire the Pb2+ and Mn2+ ion concentrations.

**NMR.** 1H spectra were recorded on a GEOL-600 Fourier transformation spectrometer at 600 MHz. The chemical shifts (δ) are reported in parts per million (ppm) with respect to TMS. Short notations used are d for doublet, t for triplet, and m for multiplet.

### RESULTS AND DISCUSSION

A solution based approach was used for the synthesis of 2D nanoplates (NPLs) and nanocrystals (NCs) of Cs2PbI2Cl2. Initially, cesium carbonate and lead acetate were dissolved in 1-octadecene (ODE), oleic acid (OA), and oleylamine (OAm) at 130 °C under an inert atmosphere in a three-necked round-bottom flask. Subsequently, benzoyl halides were swiftly injected into the reaction flask at 160 °C. The as-synthesized product (~10 mg) was thoroughly washed with hot toluene (10 mL each time) for 2–3 times and used for further characterization.

To synthesize the pure phase of Cs2PbI2Cl2, various reaction conditions were attempted. For example, at first, the reaction flask was kept for 1 h for the formation of Cs- and Pb-oleate and then benzyl halides were swiftly injected at three different temperatures of 150, 160, and 200 °C. We observed that the product was nearly pure at 160 °C, while Cs2PbCl4 was also formed along with Cs2PbI2Cl2 phase at other temperatures (Figure S2a, Supporting Information). Then, we have varied the reaction time for the first step, i.e., the formation of Cs-oleate and Pb-oleate from cesium carbonate and lead acetate (Figure S2b, Supporting Information). We observed that maintaining the first step of the reaction for 2 h at 130 °C followed by injection of benzyl halide at 160 °C was the ideal condition for the synthesis of pure all-inorganic RP phase of Cs2PbI2Cl2 (Figure 1c). The morphologies of the final products are NPLs and NCs depending upon the amount of the OA and OAm. Hence, temperature, reaction time, and concentration of capping agent play a crucial role to synthesize pure phase of Cs2PbI2Cl2 (Figure S2c, Supporting Information).

Further, we have synthesized micrometer-sized particles of Cs2PbI2Cl2 by the antisolvent method at room temperature (Figure 1d, and Scheme 1E). In a typical synthesis, CsI and PbCl2 were dissolved in DMSO and DMF solvents. Then, the solution was injected swiftly into toluene at room temperature, which leads to immediate formation of Cs2PbI2Cl2 micrometer-sized particles. We have also synthesized bulk powders of Cs2PbI2Cl2 by liquid assisted mechanochemical grinding (LAG) in DMF and EtOH solvents, starting with stoichiometric ratio of CsI and PbCl2 as precursors at room temperature, which can yield gram scale (~1 g) quantities of Cs2PbI2Cl2 (Figure 1e, and Scheme 1D). In the presence of EtOH solvent, impurity phases were detected from the PXRD pattern, which appear from the unreacted PbCl2. On the other hand, the pure phase of Cs2PbI2Cl2 was obtained using DMF solvent (Figure S3, Supporting Information).

PXRD patterns of NCs and NPLs, agglomerated microparticles, and the bulk powders synthesized by hot injection, antisolvent, and LAG methods, respectively, have been indexed based on the pure phase of tetragonal Cs2PbI2Cl2 (space group I4/mmm), as shown in Figure 1f. Cs2PbI2Cl2 adopts K2NiF4 structure that is n = 1 in the Cs2n+1PbnX3n+1 RP phase. The 2D layers were formed by corner sharing Pbl2Cl4− octahedra, in which I− ions occupy axial sites whereas Cl− ions occupy the equatorial sites. A unit cell and individual octahedron were shown in Figure 1b. The monovalent Cs+ cations are distributed between the layers of the structure (Figure 1a,b).

Transmission electron microscopic (TEM) images of the sample, synthesized by using 0.5 mL of OA and OAm, confirmed the formation of the NPLs with an average size of 500 nm (Figure 2a,b), whereas NCs with an average size of 17.4 ± 0.5 nm were formed when 1 mL of OA and OAm was used (Figure 2c,d and size distribution in Figure S4, Supporting Information). The d-spacing values for NPLs and NCs were measured as 0.935 and 0.54 nm, which indicated the (002) and (101) planes of Cs2PbI2Cl2, respectively, as shown in the HRTEM (Figure 2c and Figure 2f, respectively). The selected area electron diffraction (SAED) pattern confirmed the formation of tetragonal crystal structure and single crystalline nature (inset of Figure 2c and Figure 2f). Lower concentration of the capping agent (OA and OAm) favors the formation of large NPLs, while at higher concentration of capping agent leads to small sized NCs, which indicate that the concentration of the capping agent plays a critical role in controlling the size of Cs2PbI2Cl2 nanostructures. Strong binding of the capping agents at their higher concentration prevents the growth of the NCs and results in smaller sized NCs. Conversely, these NCs grow more along the ac-plane at lower concentration of capping agent and lead to the formation of larger NPLs.35 Further, the morphology of NPLs was explored by field emission scanning electron microscopy (FESEM), which revealed stacked plate-type of morphology (Figure S5, Supporting Information). However, Cs2PbI2Cl2 synthesized by antisolvent methods at room temperature shows agglomerate microparticles, as shown in Figure S6, Supporting Information.

Optical properties of these materials were investigated via electronic absorption and photoluminescence (PL) spectroscopy at room temperature (Figure 3). The excitonic absorption peaks appeared at 414, 415, and 419 nm for NPLs, NCs, and agglomerated microparticles, respectively (Figure 3a–c). Excitonic peak feature is the characteristic of 2D perovskite halides.36 The photoluminescence study shows a PL peak around 425 nm, when excited at 380 nm for Cs2PbI2Cl2 NCs, NPLs, and agglomerate microparticles (Figure 3a–c, respectively). However, the intensity of the PL emission of agglomerated microparticles synthesized by antisolvent method can be enhanced with adding extra surfactant (OAm) (Figure S7, Supporting Information). The enhancement of the PL emission by OAm may be due to partial passivation of the trap states.36 Optical properties of bulk Cs2PbI2Cl2 powder were measured by solid state diffuse reflectance spectroscopy (Figure 3d). Sharp adsorption edge with excitonic peak around 410 nm was observed for the solid powder sample, which matches well with the optical absorption data of single crystal Cs2PbI2Cl2 reported by the Kanatzidis group.30 However, a broad PL band exhibits at 459 nm when
Figure 3. Optical absorption (black) and PL (red) spectra of (a) Cs$_2$PbI$_2$Cl$_2$ NCs (b) Cs$_2$PbI$_2$Cl$_2$ NPLs, and (c) Cs$_2$PbI$_2$Cl$_2$ agglomerate microparticles in solution. (d) Solid state electronic absorption (a/S) and PL of bulk powder of Cs$_2$PbI$_2$Cl$_2$. (e) PL spectra of Cs$_2$PbI$_2$Cl$_2$ NCs at 298 and 77 K. (f) PL decay profile of Cs$_2$PbI$_2$Cl$_2$ NCs at 298 and 77 K.

Excited at 380 nm (Figure 3d). In the solid-state optical spectra, broadening in PL spectra is mainly attributed to the presence of defects states.

To acquire further understanding into the excitonic feature of photogenerated charge carriers of Cs$_2$PbI$_2$Cl$_2$ NCs and their dynamics, we performed PL measurements at 77 K. It has been evidenced from Figure 3e that the PL peak is red-shifted and broadened at 77 K compared to the room temperature PL. The Cs$_2$PbI$_2$Cl$_2$ NCs at room temperature unveils narrow band emission at 425 nm. At 77 K, an additional broad-band emission is observed centered at ∼440 nm along with the free excitonic (FE) peak at 428 nm (Figure 3e). The low-temperature PL results imply that the electron–phonon coupling is reasonably strong and exhibit phonon-assisted self-trapped exciton (STE) recombination, which is responsible for the broad PL band. The blue-shifted PL at room temperature with respect to PL at 77 K is contemplated to arise from the electron–phonon coupling. The STE emission at 77 K is also observed earlier for low-dimensional lead halides.

Figure 3f exemplifies the PL decays of NCs at room temperature, which can be fitted well by a biexponential function with an average lifetime ($\tau_{avg}$) of 4.39 ns comprising long-lived ($\tau_1 = 4.8$ ns) and short-lived components ($\tau_2 = 0.27$ ns) with relative amplitudes of 36% and 64%, respectively. On the other hand, the $\tau_{avg}$ of NCs was found to be 20.17 ns at 77 K, involving long-lived ($\tau_1 = 20.22$ ns) and short-lived components ($\tau_2 = 1.65$ ns) with relative amplitudes of 97% and 3%, respectively. The longer excitonic emission lifetime of the NCs at low temperature might be due to the trapping of excitonic charge carriers at liquid N$_2$ temperature.

In the ever-growing field of halide perovskites, post-synthetic chemical transformation signifies an innovative strategy to alter the stoichiometry, morphology, and optical properties. Recently, Cs$_2$PbX$_6$ has been post-synthetically transformed to brightly emitting CsPbX$_4$ NCs by water-triggered reaction or by thermal annealing, whilst thiourea-assisted post-treatment method was established for the synthesis of ultrathin CsPbX$_4$ nanowires (NWs) from CsPbBr$_3$ nanocubes. 3D cubic CsPbBr$_3$ nanocrystals have also been transformed to 2D CsPbBr$_3$ nanosheets by addition of excess PbBr$_2$. We performed post-synthetic chemical transformation to synthesize 3D CsPbBr$_3$ disk-shaped particles and 0D Cs$_4$PbCl$_6$ NCs from presynthesized 2D RP Cs$_2$PbI$_2$Cl$_2$ NCs at room temperature. Metal halides (PbBr$_2$ or MnCl$_2$) were found to play a vital role for these post-synthetic chemical transformation reactions. From 2D Cs$_2$PbI$_2$Cl$_2$ to 3D CsPbBr$_3$ transformation, first PbBr$_2$ precursor solution was prepared in 1-octadecene (ODE) solvent in the presence of capping agent at 120 °C. Then, toluene-dispersed Cs$_2$PbI$_2$Cl$_2$ was injected swiftly into PbBr$_2$ solution at room temperature, which led to the immediate formation of strongly green fluorescent CsPbBr$_3$ NCs. Similarly, MnCl$_2$ plays a vital role in the post-synthetic transformation of 0D Cs$_2$PbCl$_4$ from 2D Cs$_2$PbI$_2$Cl$_2$ at room temperature. The driving force for this transformation to the lower dimensionality may be due to the presence of excess chloride ions from MnCl$_2$, which stabilized the 0D phase of Cs$_2$PbCl$_4$.

The transformed nanostructures were further characterized by PXRD. CsPbBr$_3$ exists in two different crystalline phases, i.e., orthorhombic and cubic, which can be distinguished by the characteristic peak around 2θ = 30° (Figure S8, Supporting Information). The PXRD pattern of the transformed CsPbBr$_3$ NCs is well matched with the diffraction pattern of orthorhombic phase (Pbnm) (Figure 4a). The PXRD of Cs$_2$PbCl$_4$ NCs can be indexed with its rhombohedral phase (R3ch) (Figure 4b). TEM of CsPbBr$_3$ shows disk-like morphology of average size of ∼200 nm (Figure 4c). The morphology of Cs$_4$PbCl$_6$ was well-defined square-type with average size of ∼20 nm (Figure 4d). The SAED pattern confirmed that the synthesized CsPbBr$_3$ and Cs$_4$PbCl$_6$ were single crystalline in nature (Figure 4c,d insets). The transformed 3D CsPbBr$_3$ NCs and 0D Cs$_4$PbCl$_6$ NCs exhibit different optical properties compared to the 2D Cs$_2$PbI$_2$Cl$_2$ NCs. The absorption peak of CsPbBr$_3$ was exhibited at 493 nm, and PL emission peak was noticed at 515 nm, when excited at 480 nm (Figure 4e), whereas the emission peak of Cs$_2$PbCl$_4$ was observed at 360 nm, when excited at 300 nm (Figure 4f). Cs$_4$PbCl$_6$ has an indirect band gap; hence the emission of Cs$_4$PbCl$_6$ was probably due to the Frenkel excitons, self-trapped by the PbCl$_4^{-}$ octahedrons, as reported previously.

Furthermore, Mn$^{2+}$ was doped at the Pb$^{2+}$ site of Cs$_2$PbI$_2$Cl$_2$ NCs. Exciton energy transfer to Mn$^{2+}$ states depends upon the host band gap and relative position of $T_1$ and $A_2$ of Mn$^{2+}$-49,50 The band gap of Cs$_2$PbI$_2$Cl$_2$ is appropriate for the exciton energy transfer of Mn(II) $d-d$ transition. The synthesis of Mn-doped Cs$_2$PbI$_2$Cl$_2$ was carried out in a similar hot-injection method. In a typical synthesis, cesium carbonate, lead acetate, and manganese acetate were dissolved in ODE, OA, and OAm at 130 °C under an inert atmosphere in a three-necked round-bottom flask followed by the addition of benzyol halides into
The electronic absorption spectra of Mn \( 2^+ \) doped sample comparison to the room temperature emission (Figure 5d). Emission peak for both excitonic and dopant emissions in at 77 K also revealed red-shifted and line width broadened spectra showed strong and broad d
Cs\(_2\)Pb\(0.95\)Mn\(0.05\)I\(_2\)Cl\(_2\) (Figure 5b inset).

Crystal structure with single crystalline nature of shown in Figure 5b, which also showed the plate-type of morphology. The SAED pattern confirmed the tetragonal crystal structure with single crystalline nature of Cs\(_2\)Pb\(_{1-x}\)Mn\(_x\)I\(_2\)Cl\(_2\). TEM image with SAED pattern (inset) of (c) 3D CsPbBr\(_3\) and (d) 0D CsPbCl\(_4\).

The reaction flask at 160 °C. The as-synthesized product was thoroughly washed with hot toluene 2–3 times and used for further characterization. The concentrations of Mn\(^{2+}\) in Cs\(_2\)Pb\(_{1-x}\)Mn\(_x\)I\(_2\)Cl\(_2\) samples were investigated via ICP analysis, which are found to be 2% and 5% (Table S2, Supporting Information). PXRD pattern of Cs\(_2\)Pb\(_{1-x}\)Mn\(_x\)I\(_2\)Cl\(_2\) could be indexed based on the pure phase of tetragonal CsPbI\(_2\)Cl\(_2\) structure (space group I4/mmm) with the minor higher angle shift in 2θ value, as the ionic radii of Pb\(^{2+}\) and Mn\(^{2+}\) were 133 and 97 pm, respectively (Figures 5a and S9, Supporting Information). The TEM image of Cs\(_2\)Pb\(_{0.95}\)Mn\(_{0.05}\)I\(_2\)Cl\(_2\) was shown in Figure 5b, which also showed the plate-type of morphology. The SAED pattern confirmed the tetragonal crystal structure with single crystalline nature of Cs\(_2\)Pb\(_{0.95}\)Mn\(_{0.05}\)I\(_2\)Cl\(_2\) (Figure 5b inset).

Figure 5c represents the PL spectra of Cs\(_2\)Pb\(_{1-x}\)Mn\(_x\)I\(_2\)Cl\(_2\) (where x = 0%, 2%, and 5%) at room temperature. The PL spectra showed strong and broad d–d (\( ^{5}T_2 \) to \(^{6}A_1 \)) emission at 585 nm along with the host emission at 422 nm, when excited at 380 nm. Low-temperature PL of Cs\(_2\)Pb\(_{0.95}\)Mn\(_{0.05}\)I\(_2\)Cl\(_2\) NCs at 77 K also revealed red-shifted and width broadened emission peak for both excitonic and dopant emissions in comparison to the room temperature emission (Figure 5d).

The electronic absorption spectra of Mn\(^{2+}\) doped sample remained similar as undoped sample as shown in Figure S10 (Supporting Information). To investigate the origin of this emission, photoluminescence excitation (PLE) spectra were recorded at room temperature (Figure S11, Supporting Information) by monitoring PL at 585 nm. The PLE spectra follow the absorption spectra, which implies that both emissions (exciton and dopant emission) originated from the same absorption. Figure S12 (Supporting Information) illustrates the Mn d–d emission decay curves at room temperature and 77 K. The PL decay of Cs\(_2\)Mn\(_{0.95}\)Mn\(_{0.05}\)I\(_2\)Cl\(_2\) NCs was well-fitted by triexponential function with a lifetime of 1–2 ms, when emission was collected at 590 nm (Figure S12a and Table S3, Supporting Information), and the lifetime was found to be 1–5 ns, when emission was collected at 430 nm (Figure S12b and Table S3, Supporting Information), at room temperature. The longer lifetime emission was mainly attributed to the forbidden Mn\(^{2+}\) d–d transition. Hence, the forbidden Mn\(^{2+}\) emission was sensitized by the host CsPbI\(_2\)Cl\(_2\) following the energy transfer mechanism, which clearly reveals the successful doping of Mn\(^{2+}\) in CsPbI\(_2\)Cl\(_2\) NCs. The lifetime components for excitonic emissions increased at 77 K compared to room temperature for Mn doped sample. The dopant emissions from CsPbI\(_2\)Cl\(_2\) NCs synthesized from the benzyl halide are similar to that of the earlier synthesized CsPbI\(_2\)Cl\(_2\) using mixed oleylammonium chlorides and iodides, apart from the number of lifetime components. The additional lifetime component may arise from the probable surface defect states, which further leads to the variation in PL quantum yield (PLQY) values compared to earlier reported Mn\(^{2+}\) doped CsPbI\(_2\)Cl\(_2\) NCs. The absolute PLQY of Cs\(_2\)PbI\(_2\)Cl\(_2\) NCs was found to be 0.02%, whereas 5% Mn-doped CsPbI\(_2\)Cl\(_2\) NCs showed an enhanced PLQY of 0.97%. Earlier Manna and co-workers also observed a similar low PLQY (<0.1%) of all-inorganic RP phase of lead halide perovskite NCs.

Finally, the thermal photoluminescence characteristics and thermal stability of CsPbI\(_2\)Cl\(_2\) NCs have been systematically verified, which are essential for their practical utility. The temperature-dependent PL spectra under 380 nm excitation in the temperature range of 25–85 °C with an interval of 10 °C were recorded (Figure 6a). The decrease of PL emission intensity with increasing temperature up to 85 °C with respect to its initial PL intensity at 25 °C, as evidenced from the inset of Figure 6a, might be due to the thermal dissociation of electron–hole pair and consequent diminution of the excitonic population along with the thermally activated charge carrier.
respectively, in the solution at room temperature. Finally, Mn2+ is found to be comparable with the low-dimensional halides52 linear relationship between \( \ln(\text{correlation coefficient}) \) and temperature, respectively. The morphologies of the Cs2PbI2Cl2 were varied from NPLs to NCs with varying concentrations of capping agents, wherein a higher concentration of capping agents leads to a lower number of NPLs. All-inorganic RP phase of 2D Cs2PbI2Cl2 was synthesized by chemical grinding and antisolvent method, respectively, which were found to be promising for post-synthetic transformation to 3D CsPbBr3 and 0D Cs4PbCl6 compounds in both nano and bulk forms, post-synthetic chemical transformation, doping, and its subsequent effect on the structure–optical property relationships. In summary, flexibility and versatility of our synthetic strategies will permit the forthcoming advancement of 2D all-inorganic halides in nanodimensions and could be exploited in the field of solar cells, photodetectors, and optoelectronics.

**CONCLUSIONS**

All-inorganic RP phase of 2D Cs2PbI2Cl2 was synthesized by the solution based hot-injection method using benzoyl halides as halide precursors. The morphologies of the Cs2PbI2Cl2 were varied from NPLs to NCs with varying concentrations of capping agents, wherein a higher concentration of capping agents favors the formation of NCs. Further, the scalable quantity (~1 g) of bulk powder and micrometer-sized particles of Cs2PbI2Cl2 were synthesized via liquid assisted mechano-chemical grinding and antisolvent method, respectively, which is important in terms of the application point of view. Optical properties of both NPLs and NCs revealed typical excitonic features related to the 2D layered structure. Further, the post-synthetic transformation to 3D CsPbBr3 and 0D Cs2PbI2Cl2 from 2D RP phase was achieved by adding PbBr3 and MnCl2, respectively, in the solution at room temperature. Finally, Mn2+ was doped at the Pb2+ site of Cs2PbI2Cl2 NCs, where the successful doping was confirmed by optical property study. The PL spectra exhibited Mn2+ d-d (\( ^{6}T_{1} \) to \( ^{6}A_{1} \)) emission at 585 nm along with the host emission at 422 nm, and the longer lifetime further suggests the forbidden nature of the Mn2+ d-d transition. The line widths, peak energies, and lifetimes of PL emissions as a function of temperature were discussed in detail. Low-temperature PL experiments at 77 K for both undoped and Mn-doped NCs suggest strong electron–phonon coupling along with the evolution of phonon-assisted self-trapped exciton. Superior thermal stability was evidenced from the high temperature PL and TGA analysis for RP phase nanostructured samples. These findings result in a prominent advancement toward the synthesis of all-inorganic halide RP compounds in both nano and bulk forms, post-synthetic chemical transformation, doping, and its subsequent effect on the structure–optical property relationships. In summary, flexibility and versatility of our synthetic strategies will permit the forthcoming advancement of 2D all-inorganic halides in nanodimensions and could be exploited in the field of solar cells, photodetectors, and optoelectronics.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.9b02439.

1H NMR spectra, PXRD patterns, additional TEM images, FESEM image, absorption spectra, PL decay profile, PL and PLE spectra, Arrhenius-type plot from LPL, tables of elemental analysis results, 1H NMR \( \delta \) values, and lifetime data (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank Nanomission, DST, and Sheik Saqr Lab. P.A. and K.K acknowledge support from UGC Graduate Research Fellowships and SERB National Postdoctoral Fellowship (PDF/2018/001143), respectively. We acknowledge Swadhini Garain, JNCASR, for helping with fluorescence lifetime measurements.

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