Exploration of Near-Infrared-Emissive Colloidal Multinary Lead Halide Perovskite Nanocrystals Using an Automated Microfluidic Platform

Ioannis Lignos,†,§ Viktoriia Morad,†,‡,§ Yevhen Shynkarenko,†,§ Caterina Bernasconi,†,§ Richard M. Maceiczyk,† Loredana Protesescu,§,§ Federica Bertolotti,¶,∥ Sudhir Kumar,¶ Andrew J. deMello,†,‡,§,※ and Maksym V. Kovalenko※,†,§

†Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, Zürich 8093, Switzerland
‡Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, Zürich 8093, Switzerland
§Dipartimento di Scienze e Alta Tecnologia and To.Sca.Lab, Università dell’Insubria, Via Valleggio 11, I-22100 Como, Italy
¶Aarhus Institute of Advanced Studies (AIAS), Aarhus University, Høegh-Guldbergs Gade 6b, 8000 Aarhus C, Denmark
※Istituto di Cristallografia, Consiglio Nazionale delle Ricerche, and To.Sca.Lab, via Valleggio 11, I-22100 Como, Italy

Supporting Information

ABSTRACT: Hybrid organic—inorganic and fully inorganic lead halide perovskite nanocrystals (NCs) have recently emerged as versatile solution-processable light-emitting and light-harvesting optoelectronic materials. A particularly difficult challenge lies in warranting the practical utility of such semiconductor NCs in the red and infrared spectral regions. In this context, all three archetypal A-site monocationic perovskites—CH₃NH₃PbI₃, CH(NH₂)₂PbI₃, and CsPbI₃—suffer from either chemical or thermodynamic instabilities in their bulk form. A promising approach toward the mitigation of these challenges lies in the formation of multinary compositions (mixed cation and mixed anion). In the case of multinary colloidal NCs, such as quinary CsxFAxFAᴵ Pagination error

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Lead halide perovskites (LHP) of the APbX₃ type, where A can be methylammonium (MA, CH₃NH₃⁺), formamidinium (FA, CH(NH₂)₂⁺), inorganic cations (Cs⁺, Rb⁺), or a
mixture thereof and X is a halide (Br, I, and their mixtures), have attracted enormous attention after they were recognized as efficient thin-film absorber materials for photovoltaics, with power conversion efficiencies of up to 22.7%.1−4 Recently, there has been a surge of studies on the nanoscale counterparts of these perovskites and, in particular, on colloidal nanocrystals (NCs),5−12 which hold great promise as versatile photonic sources for displays, lighting, light-emitting diodes (LEDs), and lasers13−16 and as light harvesters for solar cells and photo-detectors.11,17 Unlike other forms of APbX3 perovskites—bulk single and polycrystals, thin films, and other substrate-grown structures—colloidal NCs have a particular set of advantages, foremost of which is their versatile solution processability and miscibility with other materials, as well as access to quantum-size effects and their facile surface- and shape-engineering.18 To date, essentially all work on colloidal APbX3 NCs has concentrated on those compositions, which emit in the visible region of the electromagnetic spectrum (between 400 and 700 nm), with CsPbBr3 and FAPbBr3 NCs, exhibiting green photoluminescence (PL) between 500 and 550 nm, being far by the most popular targets. This can be attributed to the high durability of these bromides, as compared to other compositions in the APbX3 family.

In the current study, we focus our attention on multinary perovskite NCs of the quinary composition CsxFAY1−xPb(1−y)Bry, with a view to controlling their optical properties in the near-infrared (700−800 nm). It should be noted that there is extensive literature regarding red and near-infrared emissive colloidal MAPbI3 NCs, refs 7 and 19−23 being representative examples. However, MAPbI3 NCs suffer from severe instabilities caused by humidity, light, and heat and eventually decompose into CH3NH2, PbI2, HI, and I2.12,24,25 Fully inorganic CsPbX3 NCs (X = Cl, Br, and I), synthesized by a hot injection method, exhibit tunable emission between 410 and 700 nm and high PL quantum efficiencies (50−90%).6 Presently, CsPbX3 NCs are the focus of attention with respect to their chemical engineering (i.e., identification of precursors, growth kinetics, shape-control, post-synthetic reactivity, and up-scaling),4,20,26−45 surface chemistry,8,46−50 photophysics (single-dot spectroscopy, lasing, etc.),51−59 and applications in television displays,60−62 light-emitting devices,50,63−68 and solar cells.17 The usability of red-emissive CsPbX3 NCs is, however, strongly limited by the phase instability of the 3D polymorphs of CsPbI3. For similar reasons, iodide-rich CsPb(Br/I)3 compositions, the structural chemistry of these perovskites must be considered: only those polymorphs of APbI3 compounds that retain three-dimensional (3D) corner-shared interconnections of lead halide octahedra are potent semiconductors. The extended electronic structure in lead halide perovskites arises from the periodic 3D network of PbX6 octahedra. Low-dimensionality polymorphs of the same composition exhibit higher (by at least 1 eV) and often indirect band gaps, typically on the order of 300−500 nm. 3D polymorphs of all archetypal ternary APbI3 compounds have stability issues. MAPbI3 is chemically unstable, whereas the 3D polymorphs of CsPbI3 and FAPbI3 are thermodynamically metastable and undergo transitions into 1D polymorphs (Figure 1e).76,80−85 Interestingly, the thin-film and nanoscale forms of CsPbI3 and FAPbI3 exhibit extended but still finite stability in their 3D
As for colloidal NCs, we recently reported the synthesis of a mixed-cationic composition, Cs$_x$FA$_{1-x}$PbI$_4$ with the same crystal structure as orthorhombic 3D $\gamma$-CsPbI$_3$ via a flask-based process. Multiple variations of the Cs:FA reagent ratio and synthesis temperatures led to the same composition (with ca. 10% FA). From these studies, it can be surmised that the exploration of complex compositions is prohibitively difficult via flask-based syntheses. This is because with one iteration of only one parameter per synthesis (each lasting several hours when conducted manually) several years will be required to properly map compositional space and other factors, such as the effects of ligands, solvents, and solvation equilibria.

**Experimental Design and Combinatorial Strategy.** Microfluidic reactors allow for the addition of multiple reagents in a user-defined manner, rapid thermal and mass transfer, and quantitative kinetic investigation of reactions, thus defining an ideal medium for preparing semiconductor NCs with well-defined morphologies and physicochemical properties. In addition, the advances in robust microfluidic configurations, real-time detection methods, and ligand-exchange systems, and optimization algorithms make microfluidic reactors ideal for the detailed investigation of rapid and complex reaction kinetics and for the discovery of multicomponent semiconductor NCs. Herein, we modified and applied a previously developed microfluidic platform that had been used for the synthesis and real-time characterization of binary halide NCs, and CsPbX$_3$ NCs. This platform (see Figure 2 and associated description in the Methods section) incorporates a multiphase microfluidic reactor with integrated PL and absorption detection to rapidly screen reaction conditions. The controlled injection of precursor solutions (Cs-oleate, FA-oleate, PbX$_2$, and PbY$_2$) and carrier fluid is performed in an automated manner (using syringe pumps), allowing for the formation of nanoliter droplets using a seven-port manifold and efficient mixing of precursors (in ~300 ms). In the case of Cs$_x$FA$_{1-x}$PbI$_3$ (X = Br and I) NCs, we defined four independent molar ratios, which were adjusted during synthesis: FA/Pb, Cs/Pb, Br/I, and Cs/FA. In this report, the latter is presented as the Cs percentage relative to the FA content. A tube-based microfluidic reactor allows for rapid heating of the droplets (within a few hundred ms), along with the real-time extraction of PL and absorption characteristics at various reaction times (0.1–20 s) and temperatures (25–130 °C). Additional characterization of the synthesized NCs by transmission electron microscopy (TEM) and XRD was conducted in an off-line manner, by collecting a sufficient quantity of the sample during synthesis at a fixed set of reaction conditions (see the Methods section for details). The optimized parameters were then transferred to conventional flask-based reactions.

**Synthesis of Cs$_x$FA$_{1-x}$PbI$_3$ NCs.** In our previous study, we showed that FAPbI$_3$ NCs can grow even at room temperature, while CsPbI$_3$ NCs with a 3D phase are formed at temperatures above 100 °C. Accordingly, we decided that analyzing the temperature range suitable for the formation of Cs$_x$FA$_{1-x}$PbI$_3$ NCs was an important initial task. Figure 3a–c report the variation in emission line width and PL peak at 25–130 °C (FA/Pb = 9.3, Cs/Pb = 0.3, and %Cs = 3.0). The formation of FAPbI$_3$ NCs takes place at room temperature, which can be inferred by the emergence of the PL peak at 792 nm, consistent with a previous flask-based synthetic study, in which 15 nm FAPbI$_3$ NCs exhibited a PL peak at 780 nm. However, higher temperatures led to a rapid increase in the band-gap energy, which we attribute to the...
incorporation of Cs. The possibility of smaller NC sizes (quantum dots 3−10 nm in diameter) causing larger band gaps can be discounted using postsynthesis TEM images, with all NCs obtained in this study for growth times greater than 7 s being 15−20 nm in size. Size evolution occurs very quickly and over the course of several seconds. From 50 to 90 °C, the PL peak remained stable at 740−745 nm (Figure 3c), but with a gradually decreasing fwhm. Higher synthesis temperatures (>110 °C) resulted in PL peaks closer to 700 nm, most likely due to the formation of ternary CsPbI₃ NCs with or without minimal...
incorporation of FA ions. Accordingly, we concluded that the 50–90 °C range is ideal for compositional engineering purposes.

The high speed of formation of Cs$_{0.02}$FA$_{0.99}$PbI$_3$ NCs is on par with FAPbX$_3$ (see ref 78 and Figure S1) and CsPbI$_3$ (reported previously), taking only a few seconds to stabilize the PL maximum at 740 nm and the fwhm at 52 nm (Figure 3d–f). Off-line optical characterization after synthesis indicates that there is no subsequent growth or other form of evolution in the Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs (see Figure S2). Based on these observations, further rapid automated screening, at a rate of 100 adjustments per synthesis parameter per hour, was carried out with reaction times of at least (and typically) 7 s.

The efficiency of Cs incorporation is expected to depend not only on temperature but also on the solvation conditions and Cs/FA ratio and to some extent on the Cs/Pb and FA/Pb ratios. Because these relationships are not fully and rationally predictable when the equilibrium constants and involved energies (lattice energies for all compositions, solvation energies, surface energies, and ligand binding energies) are not completely known, they were tested in this study in a combinatorial fashion (Figures S3–S6). In brief, for excess FA (by a factor of 6 with respect to Pb), a narrow fwhm can be obtained (Figure S3). At much higher FA/Pb ratios (>13), the crystal phase of the NCs tends to change from black to yellow within hours of synthesis. The TEM images revealed severe morphological irregularities in such NCs, which were in the form of large populations of micrometer-sized needles and rods (Figure S4). Furthermore, the PL tunability of Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs was limited to Cs/Pb ratios lower than 2 and Cs loadings of ≤10% (Figure S3). Outside this window, the PL maxima were always in the range of 680–700 nm, suggesting the formation of pure CsPbI$_3$ NCs or their mixtures with other compositions (see multi-Gaussian PL lines; see Figure S3e, for Cs content equal to 23.3%) or perhaps even mixtures of various shapes. The TEM images (Figure S4, S5) illustrate how the three interlinked ratios affect the morphology of the synthesized Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs. Progressive addition of 0.3–5.2% Cs$^+$ (with respect to the FA content) continuously tunes the PL maximum from 758 to 710 nm (Figure S6), while maintaining a narrow fwhm in the range of 48–55 nm. Although the XRD results suggest that mixed perovskites adopt a structure similar to that of pure FAPbI$_3$ (Figure S7), the majority of Cs$_{x}$FA$_{1-x}$PbI$_3$ NC samples exhibited low colloidal and chemical stabilities, except those samples with both low FA/Pb ratios (≤7) and low Cs loadings (up to 2%).

**Synthesis of Cs$_{x}$FA$_{1-x}$Pb(Br$_{1-y}$I$_y$)$_3$ NCs.** The addition of Br into the system was then explored as a way of stabilizing crystal structure and tuning the PL maximum in the desired range (700–800 nm). The operating temperature and reaction times were similar to those used for the synthesis of Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs. As the addition of a second halide further increases the complexity of the synthetic system and can shift the product equilibrium toward other perovskite compositions, parametric screening must be performed with caution. We therefore broadly explored the influence of the interdependent molar ratios of Cs/Pb, FA/Pb, and Br$^-$ content on the optical properties and stability of the Br/I mixtures (as illustrated in Figures S8–S10).

In brief, such a combinatorial study revealed that the parametric zones of the FA/Pb and Cs/Pb molar ratios, able to tune the PL peak between 690 and 780 nm (while maintaining a satisfactory fwhm), were 2.5–6.0 and 0.01–0.04, respectively (Figure S9). In addition, Br loading of up to 15% leads to a linear blue shift of the emission band at all FA/Pb molar ratios (Figure S10). A key message here is that in nearly all optimized compositions Br addition does not alter the emission line width or emission intensity, suggesting that the synthesized NCs have stable optical characteristics. Furthermore, an increase in Br$^-$ loading over 25% will deliver perovskite NCs with emission energies in the range of 650–720 nm. However, such an increase in Br$^-$ loading can trigger the formation of other perovskite structures, such as FAPb(Br$_{1-y}$I$_y$)$_3$ NCs, due to excess FA-oleate in the reaction system (Figure S11).

Figure 4a presents selected PL spectra in the range of 690 to 775 nm, with fwhm in the range of 45–65 nm. Such precise PL tuning is achieved through a systematic variation of all three interlinked molar ratios within their refined parametric zones. In particular, variation in Cs (in the range of 0.2–5.2%) and Br (between 0% and 15% of the total halide concentration) content leads to a blue shift in the in-line (i.e., postheating and when the reaction was quenched) absorption and PL spectra (Figure 4b).

Most importantly, the incorporation of up to 15% Br$^-$ into the structure of Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs increased the period of stability of the Cs$_{x}$FA$_{1-x}$PbI$_3$ NCs from several hours to several weeks (Figure S12).

**Transfer to Flask-Based Synthesis.** To assess whether the optimal parameters can be transferred to conventional
flask reactors, we carried out hot-injection synthesis of both CsFAx−xPbI3 and CsFAx−xPb(Br1−yIy)3 NCs (further details are provided in the Methods section). Briefly, to synthesize NCs with the nominal composition of Cs0.01FA0.99Pb(Br0.11I0.89)3 (Figure 5), PbI2 (55 mg, 0.12 mmol) and PbBr2 (5 mg, 0.014 mmol) were suspended in 1-octadecene (ODE, 4.6 mL), heated to 60 °C, and then dried under vacuum for 30 min. Subsequently, the reaction mixture was heated to 110 °C in a nitrogen environment, followed by the addition of dried solvents: oleylamine (OLA, 0.5 mL) and oleic acid (OA, 1.0 mL). Once the PbI2 dissolved, the reaction mixture was cooled to 80 °C. At this point, a mixture of FA oleate (4.8 mL) and Cs oleate (1.2 mL) stock solutions was injected into the reaction flask. After 5 s, the reaction was quenched. The crude solution was then centrifuged and the supernatant was discarded. The precipitate was dissolved in hexane, and the resulting solution was centrifuged once again, after which the supernatant and precipitate were separated. The particles from both fractions, supernatant and precipitate, were further washed to remove excess organic ligands (see further details in the Methods section). This synthesis procedure yielded nearly cubic NCs with a PL peak at 730 nm (Figure 5a−c), a PL fwhm of 40 nm (after isolation and purification), and a PL quantum yield (QY) of 80−89%. QY drops to ca. 50% in the solid-state form (NC film). We note that the larger fwhm values detected in-line in microfluidics can be attributed to size-fractioning that occurs during isolation and purification.

Crystal Structure. To uncover the structural details of CsFAx−xPb(Br1−yIy)3 NCs, synchrotron X-ray total scattering measurements were performed (using an octane solution of NCs in a quartz capillary, Figure 5c) at the X04SA-MS4 Powder Diffraction Beamline of the Swiss Light Source (Paul Scherrer Institute, Villigen, CH).121 A combined Rietveld and total scattering approach based on the Debye scattering equation (DSE, accounting for structure, size, and anisotropic morphology)121 was used for structural and microstructural characterization of CsFAx−xPb(Br1−yIy)3 NCs (details are provided in the Supporting Information). The analysis results suggest a cubic structure in which X− anions are disordered in four equivalent sites around the equilibrium position (inset of Figure 5c), similar to the disorder seen in FAPbI3 and FAPbBr3 NCs.69,122 The atomic displacement parameters (in the form of the Debye−Waller factor) were refined for all atoms; the anomalously high values for halides in the unsplit cubic arrangement suggest local structural disorder. The graphical outcomes of the DSE-based analysis of CsFAx−xPb(Br1−yIy)3 NCs are summarized in Figures 5c, S13, and S14. In a similar manner to CsPbX3 NCs,12 the peak positions slightly deviate from the cubic metric. Nevertheless, the hybrid NCs investigated here exhibited a different kind of structural defectiveness, which needs further investigation.

Figure 5. Optical absorption and PL spectra of CsFAx−xPb(Br1−yIy)3 NCs synthesized in conventional flask reactors, exhibiting a fwhm of 40 nm. (b) Bright-field scanning TEM (STEM) image of CsFAx−xPb(Br1−yIy)3 NCs. (c) Synchrotron XRD pattern (black) and best fit (red, 2Θ range of 0.5−130°; λ = 0.563 729 Å) for CsFAx−xPb(Br1−yIy)3 NCs, yielding a refined lattice parameter (a = 6.3296 Å) and the anionic composition. The inset illustrates the cubic perovskite structure of CsFAx−xPb(Br1−yIy)3 NCs (space group Pm3m, with y = 0.87 and x = 0), in which the perovskite framework consists of PbX6 units sharing the octahedral corners; the X− anions are disordered in four equivalent positions.
In addition, to further validate our findings, we compared the experimental data with a Pnma orthorhombic structure model (Figure S15). The Pnma structure does not reproduce the experimental peak intensities; at the same time, new peaks appear in a simulation, without having a counterpart in the experimental data, thus supporting the analysis presented in Figure S5c. To investigate the substitutional disorder between the FA+ cations, fully or nearly fully occupying the A-site of the cubic structure [FAPbI3, FAPbBr 3, and the herein studied CsFA1−xPb(Br1−yIy)3 NCs], we compared it to a solid solution model (Figure S16). The result of this analysis was that the Br/I substitution value is consistent with the PL peak position and with that estimated by X-ray fluorescence (XRF). The Cs quantity was too low to be detected by X-ray techniques; however, a small quantity of this cation (<5%) might be present in the crystal structure. Concerning the structurally refined s.o.f. value of Br (0.13), an even more robust determination (s.o.f = 0.10) was independently derived by adopting Vegard’s law, which correlates the refined lattice parameter and anionic composition of the mixed halide, CsFA1−xPb(Br1−yIy)3 (for x ≈ 0 and a = 6.3296 Å), with the two end members of the same series (FAPbI3, a = 6.3639 Å, and FAPbBr3, a = 6.0042 Å), as depicted in Figure S14. Additionally, using a standard benchtop energy dispersive XRF instrument and a calibration mixture of Pb(NO3)2 and KBr in a 5:1 ratio, the Br fraction in the title compound was calculated to be 0.16(3), corroborating the presented estimates. In addition, to assess whether the quinary compositions undergo phase separation into respective ternary compounds, we report the pattern of a mixture of FAPbBr3 (13% w/w) and FAPbI3 (87% w/w) cubic phases and compare it to a solid solution model (Figure S16). The result indicates the absence of phase segregation. Overall, we highlight that FA+ cations, fully or nearly fully occupying the A-site of the 3D perovskite framework, systematically favor the formation of a cubic structure [FAPbI3, FAPbBr3, and the herein studied CsFA1−xPb(Br1−yIy)3], whereas in CsPbX3 NCs, the smaller Cs ions favor the tilting of octahedra and the formation of orthorhombic γ-phases, even after incorporation of up to 10% FA.

Thermal stability of quinary NCs and, for comparison, FAPbI3 NCs was evaluated using thermogravimetry and differential scanning calorimetry (DSC); see Figure S17. The decomposition of both kinds of NCs occurs in a few steps. Both show a most pronounced DSC feature at 335 °C that can be attributed to the decomposition of FA cations, indicating that both materials are of similar thermal stability.

**Light-Emitting Diodes.** CsFA1−xPb(Br1−yIy)3 NCs were used to construct LEDs with the device structure depicted in Figure 6a. These LEDs were fabricated by spin coating poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) on prepatterned indium tin oxide (ITO)-covered glass substrates, followed by the spin coating of poly(1,3,5-benzinetriyl)tris(1-phenyl-1H-benzimidazole) (TPBi), 1.2 nm of lithium fluoride (LiF), and 100 nm of aluminum (Al) were sequentially evaporated on top of the emissive layer. Two different devices (1 and 2) were tested, with device 2 containing TOPAS polymer in the NC layer (TOPAS = cyclic olefin copolymer from TOPAS Advanced Polymers GmbH). LED performance was characterized by measuring current density and radiance as a function of the voltage applied between the ITO anode and Al cathode (Figure 6b) and by measuring the electroluminescence (EL) spectrum (Figure 6d). The current density of device 1 steadily increased from 8 × 10−4 mA cm−2 at 2 V to over 100 mA cm−2 at 10 V. The radiance surpassed 10−4 W sr−1 m−2 at just above 3 V and increased up to 3.9 W sr−1 m−2 at 7.5 V. The radiance, current density, and EL spectrum were then used to calculate the EQE, which describes the number of out-coupled photons per number of injected electrons. The EQE dependence on current density is shown in
Figure 6c, with a device 1 peak EQE of 5.9% at 0.1 mA cm$^{-2}$ (0.2% at 100 mA cm$^{-2}$) and a device 2 peak EQE of 4.2%. The peak EQE and turn-on voltage of >3 V are in line with our previous work, in which we investigated FAPbI$_3$ LEDs emitting at 772 nm. However, in the case of LEDs incorporating Cs$_x$FA$_{1-x}$Pb(Br$_{1-y}$I$_{y}$)$_3$ NCs, the EQE stays above 2.5% for currents up to 10 mA cm$^{-2}$. The peak radiance is also higher with quinary NCs (3.9 versus 1.54 W sr$^{-1}$ m$^{-2}$). While the low efficiency roll-off below 10 mA cm$^{-2}$ indicates a good electron–hole balance in the emission layer and excellent carrier/exciton confinement, the turn-on voltage of over 3 V is 1.3 V higher than expected from the band-gap energy of the Cs$_x$FA$_{1-x}$Pb(Br$_{1-y}$I$_{y}$)$_3$ NCs (1.7 eV), suggests that further optimization of the device architecture is needed in order to reduce the charge-injection barrier(s). The EL spectra (Figure 6d) revealed a sharp peak near 735 nm with a narrowest fwhm of 0.15 nm at 7 V for device 1 and as low as 27 nm at 8.5 V for device 2. Figures S18 and S19 present the evolution of EL spectra with increasing the voltage, for both devices. Even though device 1 showed the best EQE value of 5.9% and peak radiance of 3.9 W sr$^{-1}$ m$^{-2}$, device 2 (best EQE of 4.2%) showed a distinctly different behavior: EL peak narrowing at higher voltages (Figure S19), from an initial fwhm of 40 nm to 27 nm at 8.5 V. In device 2, the fwhm of the EL spectrum is strikingly narrower than that in the NC PL spectra in the solution (fwhm = 40 nm) and in films (fwhm = 52 nm); see Figure S20 for comparison. Together with the red shift of the EL peak position, this might indicate an efficient energy transfer between the NCs. As a plausible scenario, the applied voltage might induce anion migration and hence alter the energy band gaps of NCs within the layer. The emission might then occur through the channeling of excitation into the specific population of NCs. To the best of our knowledge, the EL fwhm of 27 nm (62 meV) is the narrowest among those reported for the red (and near-IR) perovskite LEDs. Figure S21 shows typical transient properties of the NC LED at a constant voltage of 4.5 V. Significant growth of the current density from 0.1 mA cm$^{-2}$ to over 5 mA cm$^{-2}$ within seconds is observed. This might again support the possibility of the ionic rearrangement within the NC film that improves charge injection, similar to the light-emitting electrochemical devices. The overall LED device lifetime (to reach half of the maximum EL intensity) at 4.5 V bias is about half a minute. For comparison, other perovskite LEDs in this wavelength range are those absorbing layers. In this regard, in contrast to conventional molecular LHP solutions used as inks, the ease of compositional engineering and facile ligand removal exhibited by the currently developed quinary NCs, followed by low-temperature sintering for recrystallization into continuous thin films, suggests numerous possibilities. Alternatively, or rather orthogonally, methods of surface coating for maintaining the quantum-size effects may enable thin-film or quantum-dot-like photovoltaic devices and photodetectors.

**CONCLUSIONS**

Herein, we have described the combinatorial synthesis of highly luminescent and stable Cs$_x$FA$_{1-x}$Pb(Br$_{1-y}$I$_{y}$)$_3$ NCs with emission and absorption spectra between 690 and 780 nm. Using a microfluidic platform, we identified the compositional parameter space for fine-tuning optical properties, while retaining emission line widths in the range of 45–65 nm (before isolation, size selection, and purification). Importantly, microfluidic parameters can be readily transferred to conventional flask-based synthetic processes used by the perovskite research community. The PL fwhm can be further refined to ~40 nm as a result of the size selection occurring during the isolation and purification of NCs. Characterization by synchrotron X-ray scattering indicates a cubic structure for the Cs$_x$FA$_{1-x}$Pb(Br$_{1-y}$I$_{y}$)$_3$ NCs, wherein solid mixed-anion solutions can be clearly confirmed. The distribution of Cs ions remains rather controversial, yet its addition to the reaction mixture is of paramount importance in improving the long-term stability of NCs. The successful fabrication of NC-based LED devices with EQEs as high as 5.9% indicates the excellent chemical durability of Cs$_x$FA$_{1-x}$Pb(Br$_{1-y}$I$_{y}$)$_3$ NCs. Future studies should focus on understanding the interesting observations of the slow transient response of the LEDs and narrow EL spectral line width of 27 at 735 nm.

The synthesis of mulinary lead halide perovskite (LHP) NCs might open opportunities for the broad deployment of these nanomaterials in photovoltaics and other optoelectronic devices. For instance, these infrared-active NCs are highly desirable for applications in single-junction or tandem photovoltaics, where NC colloids can be employed as inks for depositing active absorbing layers. In this regard, in contrast to conventional molecular LHP solutions used as inks, the ease of compositional engineering and facile ligand removal exhibited by the currently developed quinary NCs, followed by low-temperature sintering for recrystallization into continuous thin films, suggests numerous possibilities. Alternatively, or rather orthogonally, methods of surface coating for maintaining the quantum-size effects may enable thin-film or quantum-dot-like photovoltaic devices and photodetectors.

**METHODS**

**Materials.** Cesium carbonate (Cs$_2$CO$_3$, Aldrich, 99.9%), formamidinium acetate (Sigma-Aldrich, 99.9%), lead bromide (PbBr$_2$, ABCR, 98%), lead iodide (PbI$_2$, ABCR, 99.999%), 1-octadecene (99%), oleic acid (Sigma-Aldrich, 90%), and oleylamine (Acros, ≥ 96%) were used as the reagents. Galden PFPE fluid was purchased from Blaser Swisslube AG. Patterned indium tin oxide (ITO)-covered glass substrates were purchased from Lumtecht. The hole injection material PEDOT·PSS was purchased from Heraeus (CLEVIOS VP Al 4083), while the hole transport material poly-TPD was procured from Lumtecht and the electron transport material TPBi was supplied by e-Ray Optoelectronics. The electron injection material LiF was purchased from Acros Organics, and Al pellets were purchased from Kurt J. Lesker Co Ltd. TOPAS polymer (cyclic olein copolymer) was received from TOPAS Advanced Polymers GmbH. All the materials for LED production were used as received without any further purification.

**Microfluidic Synthesis.** Various concentrations of precursor solutions (see Supporting Information for details) were used depending on the experimental purpose (sample collection, absorption measurements, PL measurements). Precision syringe pumps (neMESYS, Cetoni AG) were used to inject the dispersed phase (PbX$_2$, FA-oleate, and Cs-oleate precursor solutions) and the carrier fluid (Galden fluorinated fluid, Blaser Swisslube AG, Germany) toward a manifold (Manifold Assay 7 Port 10-32 Std, Upchurch Scientific, Germany) to form a segmented flow of droplets. The injection manifold and the syringes carrying the precursor solutions were connected through polytetrafluoroethylene tubing (i.d. 250 μm, o.d. 1.16 mm, Upchurch Scientific, Germany) using polyether ether ketone finger-tight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the manifold via fluorinated ethylene propylene tubing (i.d. 750 μm, o.d. 1/16 in., Upchurch Scientific, Germany). Typical flow rates were between 80 and 100 μL min$^{-1}$ for the carrier phase and between 0.1 and 50 μL min$^{-1}$ for the precursors. The chemical payload of the formed droplets can be tuned in a precise and rapid fashion by continuously varying the precursor volumetric flow rates. The formed droplets containing the reaction mixture were subsequently directed through perfluorothether tubing (i.d. 500 μm, o.d. 1/16 in., Upchurch Scientific, Germany) coiled around a copper heating rod (diameter = 1.5 cm) to allow initiation of the NC-forming reaction and online detection of the formed perovskite NCs. The overall reaction time was kept constant in all experiments by ensuring a...
constant tubing length between the point where the tubing enters the heating rod and the detection volume.

**Online Photoluminescence Measurements.** A 375 nm LED (M357LS3-Mounted LED, Thorlabs, Germany) was used as an excitation source for PL measurements. The collimated beam was directed toward a dichroic beam splitter (Multiphoton LP-Strahleinteiler HC 375 LP, AHF, Germany) and then focused into the microfluidic channel using an aspheric lens (A240TM, f = 80 mm, NA 0.50, Thorlabs, Germany). Emission originating from the microfluidic channel was collected by the same lens, passed through the dichroic beam splitter, and coupled via a 10X objective (RMS10X, NA 0.25, Thorlabs, Germany) to a fiber spectrometer (QE 65000, Ocean Optics, UK) via a 2 m long multimode fiber with a core diameter of 400 μm (QP400-2-UV-vis, Ocean Optics, UK). The spectrometer incorporated a 20 μm entrance slit, a 600 lines/mm grating, and a 2048-pixel detector. The spectrometer was operated between 350 and 1100 nm, and data were recorded using an integration time of 100 ms.

**Online Absorbance Measurements.** Absorbance measurements were conducted after the heating stage, where the reaction mixture flows through a high-purity perfluoralkoxy capillary (1/16 in. o.d., 500 μm i.d., IDEX Health & Science, USA). The in-line absorbance spectrometer consists of a fiber-coupled halogen lamp (HL-2000 HP, Ocean Optics, UK) and a fiber-coupled spectrometer ( AvaSpec UL2048 Starline, Avantes, USA). The spectrometer was operated between 200 and 1100 nm, and data were recorded using an integration time of 100 ms.

**Flask Synthesis: Preparation of Formamidinium Olete Stock Solution.** Formamidinium acetate (3.765 mmol, 0.392 g, Aldrich, 99%) was loaded into a 50 mL three-neck flask with ODE (18 mL) and OA (12 mL). The reaction mixture was degassed three times at room temperature, heated to 120 °C in a nitrogen environment, maintained at that temperature until the reaction is complete, and then cooled to room temperature. The resulting solution was stored in a glovebox.

**Flask Synthesis: Preparation of a Cesium Olate Stock Solution.** Cesium carbonate (0.015 mmol, 5 mg) was loaded into a 25 mL three-neck flask along with ODE (10 mL) and OA (0.625 mL). The reaction mixture was degassed three times at room temperature, heated to 120 °C in a nitrogen atmosphere, maintained at that temperature until the reaction is complete, and then cooled to room temperature. The resulting solution was stored in a glovebox.

**Flask Synthesis of Cs_{0.01}FA_{0.99}Pb(Br_{0.11}I_{0.89})_3 NCs.** In a 25 mL three-necked flask, PbI₂ (55 mg, 0.12 mmol, Sigma-Aldrich) and PbBr₂ (5 mg, 0.014 mmol, Sigma-Aldrich) were suspended in ODE (4.6 mL), heated to 60 °C, and then dried under vacuum for 30 min. Subsequently, the reaction mixture was heated to 110 °C in a nitrogen atmosphere, followed by the addition of dried solvents: OLA (0.5 mL, Streum) and OA (1.0 mL, Aldrich). Once PbI₂ was dissolved, the reaction mixture was cooled to 80 °C. At this point, a mixture of the formamidinium olete (4.8 mL) and cesium olete (1.2 mL) stock solutions was injected into the reaction flask. After another 15 s, the reaction mixture was cooled using a water-ice bath. The crude solution was centrifuged at 12 100 rpm for 7 min, and the supernatant discarded. The precipitate was dissolved in hexane (250 μL), and the resulting solution was centrifuged again at 10 000 rpm for 3 min. The supernatant and precipitate were separated, and 150 μL of hexane was added to the supernatant. This fraction was labeled as “SN.” The precipitate was dissolved in toluene (1.0 mL) and centrifuged at 3500 rpm for 2 min to get rid of large NCs, with the resultant sample being labeled as “P.” Particles from both fractions were washed again to remove excess organic ligands.

**Washing of Cs_{0.01}FA_{0.99}Pb(Br_{0.11}I_{0.89})_3 SN NCs.** To 100 μL of a hexane solution of NCs were added hexane (100 μL), toluene (200 μL), and methyl acetate (530 μL). The solution was centrifuged at 13 400 rpm for 3 min and redissolved in hexane or toluene (PL at ~730 nm).

**Washing of Cs_{0.01}FA_{0.99}Pb(Br_{0.11}I_{0.89})_3 P NCs.** Methyl acetate (665 μL) was added to a toluene solution of fraction “P” and centrifuged for 3 min at 10 000 rpm. The obtained precipitate was dissolved in toluene, hexane, or octane (PL at ~750 nm).

**Offline Characterization.** Ultraviolet–visible (UV–vis) absorbance spectra were recorded using a Jasco V770 spectrometer in transmission mode. Photoluminescence spectra were recorded using a Fluoromax iHR 320 Horiba Jobin Yvon spectrophotometer equipped with a PMT detector. The excitation wavelength was 400 nm, and the excitation source was a 450 W xenon lamp. The measured intensities were corrected to account for the spectral response of the detector. Powder XRD patterns were recorded using a powder diffractometer (STOE STADI P) with Cu Kα1 radiation. The diffractometer was operated in transmission mode with a germanium monochromator and a silicon strip detector (Dectris Mythen). TEM images were captured using a JEOL JEM-2200FS microscope operated at 200 kV. Quantitative XRF measurements were conducted using a benchtop Minipal 2 PANalytical spectrometer with polycarbonate films supporting dry colloids or powders and a Cr X-ray tube operating at a maximum power of 30 W. Thermal analysis (thermogravimetry and differential scanning calorimetry) was performed using a Netzsch Simultaneous thermal analyzer (STA 449 F5 Jupiter). A powdered sample (~6–10 mg) was placed in an alumina crucible and heated under Ar gas flow (50 mL/min) to 800 °C (10 °C/min). NC solutions in hexane were predried in small alumina beakers at room temperature.

**Quantum Yield Measurements.** To measure the relative PL quantum yield of the NC solution, dilute solutions of NCs in toluene and dye standards (Rhodamine 6G in ethanol and zinc phthalocyanine in benzene) were prepared in 10 mm optical path length cuvettes, ensuring an absorbance of approximately 0.1 at either 488 or 633 nm. PL quantum yields were calculated according to

$$\Phi_i = \frac{F_i n_i}{F_s n_s} \Phi^*_s$$

where $\Phi_i$ and $\Phi^*_s$ are the PL QYs of the sample and standard, respectively; $F_i$ and $F_s$ are the absorption factors of the sample and standard ($f = 10^{-4}$, where $A$ is the absorbance), respectively; $n_i$ and $n_s$ are the refractive indices of the sample and standard, respectively.

Absolute quantum yield measurements of the films and NC solutions were performed using a Hamamatsu Quantaurus QY spectrometer (C11347-11) equipped with an integrating sphere. The excitation peak wavelength was 450 nm.

**Fabrication of LED Devices.** Initially, ITO substrates were rinsed with a mixture of deionized water and detergent solution. Subsequently, substrates were sonicated for 20 min in acetone and isopropyl alcohol. To enhance wettability, substrates were treated with an oxygen plasma for 10 min. An aqeous solution of PEDOT:PSS was spin-coated at 4000 rpm for 30 s, after which the ITO substrates were annealed on a hot plate under ambient conditions for 30 min at 130 °C. Subsequently, they were transferred into a nitrogen-filled glovebox for the deposition of subsequent layers. Poly-TPD was spin coated at 1000 rpm from a 2 mg/mL chlorobenzene solution and annealed for 20 min at 120 °C. For device 1 a colloidal suspension of Cs_{0.01}FA_{0.99}Pb(Br_{0.11}I_{0.89})_3 NCs in hexane (7 mg/mL) was spin coated at 2000 rpm; for device 2 the NC solution was mixed with TOPAS polymer (0.5 mg/mL) and spin coated at 2000 rpm. Subsequently, the substrates were transferred into a vacuum chamber at 10⁻⁶ mbar, where 50 nm of TPBI (electron transport layer), 1.2 nm of LiF, and 100 nm of Al (cathode) were evaporated through a shadow mask at vaporation rates of 0.5, 0.1, and 2 Å/s, respectively. An active pixel area of 16 mm² was determined by the overlap of ITO and Al. All devices were measured under ambient conditions without encapsulation.

**LED Performance Characterization.** The $F$–$V$–$L$ characteristics of the fabricated LEDs were measured under ambient conditions using a Keysight 2920b source measurement unit and a calibrated photodiode (FDS1010-CAL, Thorlabs). The size of the photodiode (10 × 10 mm²) is much larger than that of the active pixel size (4 × 4 mm²) of the LEDs. The EQEs of the fabricated LEDs were calculated from the known EL spectra of the LEDs and photodiode sensitivity, while the radiance was calculated assuming a Lambertian emission profile. EL spectra were recorded using a C2CS200 CCD spectrometer (Thorlabs) and a PR-655 (PhotoResearch) spectroradiometer. LED transient optoelectronic properties were measured using a Keysight 2920b source measurement unit and amplified photodiode (PDA36A-EC, Thorlabs) with 20 μs resolution.

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Synchrotron X-ray Total Scattering Measurements. The experimental synchrotron X-ray total scattering data of colloidal Cs$_x$FA$_{1-x}$(Br$_x$I$_{1-x}$) NCs ($FA = [HN(CH_3)_2]$) NCs in octane were collected at the X04SA-MS54 Powder Diffraction Beamline of the Swiss Light Source (Paul Scherrer Institute, Villigen, CH) using a certified quartz capillary (0.5 mm in diameter). The operational beam energy was set to 22 keV ($\lambda = 0.563729$ Å) and accurately determined using a silicon powder standard (NIST 640d, a$_s$ = 0.543 123(8) mm at 22.5 °C). Data were collected in the 0.5–130° 2θ range using a single-photon-counting silicon microstrip detector (MYTHEN II). Total scattering patterns with air background, empty glass capillary, and pure solvent were independently collected under the same experimental conditions and properly subtracted from the sample signal. Transmission coefficients of the sample- and solvent-loaded capillaries were also measured and used for angle-dependent absorption correction. Inelastic Compton scattering was added as an additional model component during data analysis. For DSE-based modeling, an angular range of 3–120° was used.

Temperature-dependent measurements were also performed in the range of 98–348 K using a temperature-controlled N$_2$ stream flowing over the capillary. No phase transitions were observed in the explored temperature range.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b01122.

Additional schematic illustration, preparation of precursors, synthesis procedure in a flask, TEM images, XRD patterns, and the PL and absorption spectra of Cs$_x$FA$_{1-x}$Pb$_x$I$_3$ NCs (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: maryna.bodnarchuk@empa.ch.
*E-mail: andrew.demello@chem.ethz.ch.
*E-mail: mkovalenko@ethz.ch.

ORCID

Ioannis Lignos: 0000-0002-6816-3290
Richard M. Maceczky: 0000-0001-5735-2689
Loredana Protesescu: 0000-0002-9776-9881
Federica Bertolotti: 0000-0002-6001-9040
Sudhir Kumar: 0000-0002-2994-7084
Norberto Masciocchi: 0000-0001-9921-2350
Antonietta Guagliardi: 0000-0001-6390-2114
Chih-Jen Shih: 0000-0002-5258-3485
Andrew J. de Mello: 0000-0003-1943-1356
Maksym V. Kovalenko: 0000-0002-6396-8938

Present Address
3Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States.

Notes
The authors declare no competing financial interest.

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