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Benzoyl Halides as Alternative Precursors for the Colloidal Synthesisof Lead-Based Halide Perovskite Nanocrystals

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ABSTRACT: We propose here a new colloidal approach for thesynthesis of both all-inorganic and hybrid organic−inorganic leadhalide perovskite nanocrystals (NCs). The main limitation of theprotocols that are currently in use, such as the hot injection andthe ligand-assisted reprecipitation routes, is that they employPbX_2 (X = Cl, Br, or I) salts as both lead and halide precursors.This imposes restrictions on being able to precisely tune theamount of reaction species and, consequently, on being able toregulate the composition of the final NCs. In order to overcomethis issue, we show here that benzoyl halides can be efficientlyused as halide sources to be injected in a solution of metal cations(mainly in the form of metal carboxylates) for the synthesis of$APbX_3$ NCs (in which A = Cs^+, $CH_3NH_3^+$, or $CH(NH_2)_2^+$). In this way, it is possible to independently tune the amount of bothcations and halide precursors in the synthesis. The $APbX_3$ NCs that were prepared with our protocol show excellent opticalproperties, such as high photoluminescence quantum yields, low amplified spontaneous emission thresholds, and enhancedstability in air. It is noteworthy that $CsPbI_3$ NCs, which crystallize in the cubic α phase, are stable in air for weeks without anypostsynthesis treatment. The improved properties of our $CsPbX_3$ perovskite NCs can be ascribed to the formation of lead halideterminated surfaces, in which Cs cations are replaced by alkylammonium ions.

■ INTRODUCTION Over the past few years, semiconductor metal halide nano-crystals (NCs) with a perovskite crystal structure have emergedas one of the most interesting materials for optoelectronicapplications. [1−11] In particular, lead-based halide perovskite NCswith formula $APbX_3$, in which A can be Cs^+, $CH_3NH_3^+$ (MA),or $CH(NH_2)_2^+$ (FA) and X is Cl, Br, or I, have been recentlyshown to have outstanding optical properties. [12] Suchcompounds are characterized by a broad tunable photo-luminescence (PL) that ranges from the ultraviolet (UV) tothe near-infrared region of the electromagnetic spectrum, anarrow full width at half-maximum (fwhm), and high PLquantum yields (PLQY). [7−11,13−19] Interestingly, the PLemission of such perovskite NCs can be easily adjusted notonly through size control and subsequently through quantumconfinement, as is the case for standard quantum dots but alsothrough compositional mixing, for example, via simple anion-exchange reactions.

20−27 Such properties have inspiredresearchers to exploit this class of materials for use in efficientsolar cells, sensitive photodetectors, low threshold lasers, andlight-emitting diodes (LEDs). 3,4,7,9−13 To date, various approaches have been proposed for thedirect synthesis of all-inorganic and organic−inorganic metalhalide perovskite colloidal NCs, with the hot-injection and theligand-assisted reprecipitation (LARP) ones being the mostused and most developed methods.7,9−11 The former, which was initially devised for all-inorganic perovskite NCs, is based on the hot injection (up to 200 °C) of the A cation (in theform of Cs−oleate for Cs or methylamine for MA) to a solution containing a metal halide salt (e.g., PbX_2, X = Cl, Br, I)and surfactants (e.g., oleylamine and oleic acid). 19,28−33Immediately after the injection, a rapid salt metathesis reaction occurs, forming ternary halide NC materials. Conversely, theLARP strategy, which was originally proposed for the synthesisof organic−inorganic $MAPbX_3$ NCs, but was later extended to the synthesis of all-inorganic $CsPbX_3$ systems, is performed atlow temperatures (typically from room temperature, RT, to 60°C). This method is based on the reprecipitation of halide saltsin the presence of ligands: metal halide salts (or organic halidesalts in the case of hybrid perovskites) are solubilized in one ormore polar solvents, like DMF, and are subsequently addeddropwise to a nonpolar medium, like toluene, in the presence ofligands. 2,15,18,34−40 The low solubility of halide salts in thenonpolar solvent triggers their precipitation with therecrystallization of halide NCs.

Both procedures have various limitations, the main one ofwhich is the use of inorganic salts (i.e., PbX_2) as both cationand anion precursors. Indeed, since the ratio of cations toanions employed in the synthesis is linked to that of the choseninorganic salts, it is not possible to precisely tune thecomposition of the final NCs. Furthermore, a notabledisadvantage is that it is difficult to work with an excess ofhalide ions, which is an experimental condition that has beenshown to favor the formation of lead halide perovskite NCswith improved stability and optical properties. 2,29,41The obstacles imposed by these two techniques werepartially overcome by Wei et al., who proposed an alternativecolloidal route for the preparation of $CsPbX_3$ NCs, which waslater called the "three-precursors approach". 42 Such a synthesisis based on the dissolution of Cs^+ and Pb^{2+} cations in fatty acidsfollowed by the injection of an alkylammonium halide salt (asthe halide precursor). This procedure was then adopted andrevised by Yassitepe et al. for the preparation of amine-free$CsPbX_3$ NCs for LEDs43 and by Protesescu et al. and Li et al.for the synthesis of $FAPbX_3$ (X = Br, I) NCs. 44−46 Thisapproach allows one to work with the desired stoichiometry ofthe ions, since the halide ions and the metal cation sources arenot delivered together, i.e., they are not delivered with the samechemical precursor. On the other hand, its potential versatilityis limited by the poor reactivity of the alkylammonium halidesalts (i.e., $CsPbI_3$, $CsPbCl_3$, $MAPbX_3$, and $FAPbCl_3$ NCs havenot been reported using this strategy), which can also lead tothe formation of

undesired secondary phases.In order to overcome the restrictions associated with theaforementioned synthetic procedures, we propose here a newcolloidal synthesis approach that can lead to either all-inorganicor organic–inorganic lead-based halide perovskite NCs. Thisnew approach relies on the use of benzoyl halides as halideprecursors, which can be easily injected into a solution of metalcations (such as metal carboxylates) and desired ligands (oleylamine and oleic acid). This injection immediately triggersthe nucleation and the growth of metal halide NCs (see Scheme 1). By simply tuning the relative amount of cationprecursors, ligands, solvents, benzoyl halides, and the injectiontemperature, it is possible to synthesize either all-inorganic ororganic–inorganic $APbX_3$ (A = Cs, MA or FA and X = Cl, Bror I) NCs with tight control over the size distribution and withhigh phase purity. In addition, thanks to the strong reactivity ofbenzoyl halides even at RT, they can be used for anion-exchange reactions using presynthesized $CsPbX_3$ NCs.The $APbBr_3$ NCs that were prepared using our protocol arecharacterized by their PLQYs, which were as high as 92%, andby their very low amplified spontaneous emission (ASE)thresholds. Moreover, the $APbI_3$ NCs had PLQYs of around55% and, finally, the $CsPbCl_3$ NCs exhibited a record PLQYvalue of 65%. Also, they exhibited a much higher phase stabilitythan that which has been previously reported for NCs preparedwith other synthesis methods. It is noteworthy that cubic$CsPbI_3$ NCs are stable in air for weeks without anypostsynthetic treatment, which is different from those preparedusing the classic hot-injection or LARP approaches. [28,44,47−50] The optimal properties of our $CsPbX_3$ perovskite NCs can beascribed to the formation of lead halide-terminated surfaces inwhich Cs cations are replaced by alkylammonium ions. Our X-ray photoelectron spectroscopy analysis revealed, in fact, that allour $CsPbX_3$ NCs are Cs poor and contain a considerableamount of amines, most likely in the form of oleylammoniumions. Indeed, the formation of these surfaces is favored underour synthetic conditions: the use of benzoyl halides provides ahalide-rich environment and, at the same time, an efficientprotonation of the oleylamine.
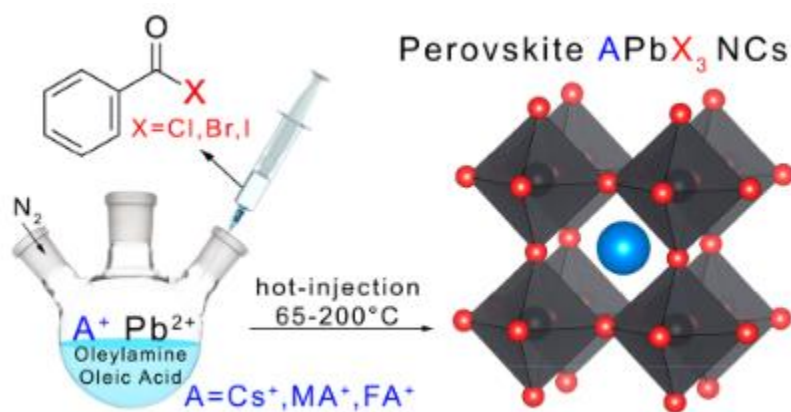
Scheme 1. Colloidal Synthesis of Lead Based HalidePerovskite Nanocrystals Using Benzoyl Halides as Halide Precursors.

■ EXPERIMENTAL SECTION Chemicals. Lead acetate trihydrate (Pb(CH3COO)2·3H2O, 99.99%), lead(II) oxide (PbO, 99.999%), sodium iodide (NaI,99.99%) cesium carbonate (Cs 2CO 3 , reagent Plus, 99%), cesiumacetate (CH 3 COOCs, 99.9%), methylamine (CH 3 NH2 , 2 M solutionin tetrahydrofuran, THF), formamidinium acetate salt (HN   CHNH 2·CH 3COOH, 99%), benzoyl bromide (C6 H5 COBr, 97%),benzoyl chloride (C 6 H 5 COCl, 98%), toluene (anhydrous, 99.5%),octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%),and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Allchemicals were used without any further purification.

Preparation of Benzoyl Iodide. The reaction was performed in aN 2 -filled glovebox following the procedure reported by Theobald andSmith. 51 In short, sodium iodide (3 g) was mixed with benzoylchloride (1.4 mL) in a 20 mL vial. The mixture was vigorously stirredat 75 °C on a hot plate for 5 h. The reaction mixture turned fromcolorless to an orange red color, indicating that the transformation ofthe benzoyl chloride into the benzoyl iodide was successful. Next, thereaction mixture was cooled down to RT and diluted using 3 mL ofanhydrous ODE. Finally, the solution was filtered, using apolytetrafluorethylene membrane filter with a 0.45 μm pore size, inorder to collect the liquid precursor. The unambiguous identificationof all of the organic species in solution as well as the reaction yield (97.7%) was possible by means of nuclear magnetic resonance (NMR, see the Supporting Information, SI, for the complete assignment andquantification of the species in the reaction mixture).

Synthesis of CsPbX 3 NCs. In a typical synthesis, cesium carbonate (16 mg), lead acetate trihydrate (76 mg), 0.3 mL of OA, 1 mL of OLAM, and 5 mL of ODE were loaded into a 25 mL 3-neck round-bottom flask and dried under vacuum for 1 h at 130 °C. Subsequently, the temperature was increased to 165−200 °C (See Table 1 for details) under N 2 , and the desired amount of the benzoyl halideprecursor was swiftly injected (0.6 mmol in the case of benzoylbromide and iodide and 1.8 mmol in the case of benzoyl chloride).The reaction mixture was immediately cooled down in an ice−water bath for CsPbBr 3 and CsPbI 3 NCs, while it was quenched after 20 s for CsPbCl 3 NCs. Finally, 5 mL of toluene was added to the crude NC solutions, and the resulting mixture was centrifuged for 10 min at 4krpm. The supernatant was discarded, and the precipitate was dispersed in 5 mL of toluene for further use.

Table 1. Synthetic Parameters Used for the Synthesis ofAPbX 3 NCs.

sample	OLAM (mL)	OA (mL)	temperature (°C)
$CsPbCl_3$	1	0.3	200
$CsPbBr_3$	1	0.3	170
$CsPbI_3$	1	0.3	165
$MAPbCl_3$	0.1	2.5	65
$MAPbBr_3$	0.025	2.5	65
$MAPbI_3$	0.150	2.5	65
$FAPbCl_3$	0.025	2.5	95
$FAPbBr_3$	0.025	2.5	75
$FAPbI_3$	0.200	2.5	95

Synthesis of Mixed CsPb(Br,Cl) 3 and CsPb(Br,I) 3 NCs. Cesium carbonate (16 mg), lead acetate trihydrate (76 mg), 0.3 mL of OA, 1mL of OLAM, and 5 mL of ODE were loaded into a 25 mL 3-neckround-bottom flask and dried under vacuum for 1 h at 130 °C.Subsequently, the temperature was increased to 170 °C under N2 , and0.6 mmol of the mixture of benzoyl chloride/bromide (a precursorratio of 1:1 led to NCs emitting at 448 nm) or benzoyl bromide/iodide (precursor ratios of 5:1 and 1:1 led to NCs emitting at 544 and594 nm, respectively) was swiftly injected. The reaction mixture was immediately cooled down in an ice−water bath. The NCs were collected by adding 5 mL of toluene to the crude solution followed bycentrifugation at 4 krpm for 10 min. The supernatant was discarded,and the precipitate was redispersed in 5 mL of toluene.

Synthesis of MAPbX 3 NCs. Lead oxide (44 mg), 2.5 mL of OA,0.025 mL of OLAM, and 5 mL of ODE were mixed in a 25 mL 3-neckround-bottom flask and dried under vacuum for 1 h at 125 °C.Subsequently, the temperature was lowered to 65 °C under N 2.Methylamine (0.170 mL) was injected, followed by the injection of0.6 mmol of the benzoyl halide precursor (see Table 1 for details). Thereaction was quenched by the addition of 5 mL of toluene after 30 s inthe case of MAPbBr 3 and MAPbI3 NCs and after 10 s in the case of MAPbCl 3 NCs. The NCs were collected by centrifuging the crudesolution at 4 krpm for 10 min.

Synthesis of FAPbX 3 NCs. Lead acetate trihydrate (76 mg),formamidinium acetate (40 mg), 2.5 mL of OA, 0.025 mL of OLAM,and 5 mL of ODE were mixed in a 25 mL 3-neck round-bottom flaskand dried under vacuum for 1 h at 125 °C. Subsequently, thetemperature was lowered to 75−95 °C (See table S1) under N 2 , and 0.6 mmol of the benzoyl halide precursor was rapidly injected. After 30s, the reaction mixture was cooled down in an ice−water bath. A 5 mL amount of toluene was added to the crude solution, and the resulting mixture was

centrifuged for 10 min at 4 krpm. FAPbI $_3$ NCs werewashed once with ethyl acetate (using a toluene/ethyl acetate ratio of5/1) and were eventually redispersed in toluene.

Anion Exchange Reactions. In short, 0.500 mL of the CsPbX $_3$NC dispersion was diluted with 2 mL of anhydrous toluene, and different amounts of a 0.12 M solution of benzoyl halide in toluene (ranging from 30 to 500 μL) were swiftly injected under vigorous stirring at RT. Finally, the NCs were collected by centrifugation at 4krpm for 10 min.

UV–vis Absorption and PL Measurements. The UV–visabsorption spectra were recorded using a Varian Cary 300 UV–visabsorption spectrophotometer. The PL spectra were measured on a Varian Cary Eclipse spectrophotometer using an excitation wavelength(λex) of 350 nm for all of the chloride and bromide samples and 450nm for all of the iodide compounds. Samples were prepared by diluting NC solutions in toluene in quartz cuvettes with a path length of 1 cm.

PL Quantum Yields and Time-Resolved PL Measurements. The samples were measured with an Edinburgh FLS900 fluorescence spectrometer equipped with a xenon lamp, a monochromator for steady-state PL excitation, and a time-correlated single-photon counting unit coupled with a pulsed laser diode (λex = 375 and 405nm, pulse width = 50 ps) for time-resolved PL. The PLQY was measured using a calibrated integrating sphere (λex = 350 nm for all of the chloride and the bromide samples and λex = 450 nm for all of theiodide samples). All solutions were diluted to an optical density of 0.1or lower (at the corresponding excitation wavelength) in order tominimize the reabsorbance of the fluorophore.

Amplified Spontaneous Emission (ASE) Measurements. All of the APbBr $_3$ (A = Cs+, MA+ , or FA+) NC samples that were used forASE dynamics were cleaned twice by precipitation using ethyl acetate(the volume ratio of toluene to ethyl acetate was 5:1) and redispersion in toluene. Eventually, thick NC films were produced on glass substrates by drop casting colloidal solutions. The NC films wereoptically excited by a pulsed laser source at λ = 405 nm, with a pulsewidth of 50 fs and a repetition rate of 1 kHz at normal incidence. The pump beam was focused on the sample by a cylindrical lens, producingan excitation stripe of about 0.6 cm in length. The emission spectrawere recorded using a collection lens and a fiber-coupled OceanOptics HR4000 spectrometer at an angle close to 90° with respect tothat of the excitation beam.

Transmission Electron Microscopy (TEM) Characterization.The samples were prepared by drop-casting dilute solutions of NCsonto carbon-coated copper grids. Low-resolution TEM measurementswere performed on a JEOL-1100 transmission electron microscope operating at an acceleration voltage of 100 kV.

X-ray Diffraction (XRD) Characterization. XRD analysis wasperformed on a PANanalytical Empyrean X-ray diffractometer,equipped with a 1.8 kW Cu Kα ceramic X-ray tube and a PIXcel 3D2 × 2 area detector, operating at 45 kV and 40 mA. Specimens for theXRD measurements were prepared by drop-casting a concentrated NCsolution onto a quartz zero-diffraction single crystal substrate. Thediffraction patterns were collected under ambient conditions using parallel beam geometry and symmetric reflection mode. XRD dataanalysis was conducted using the HighScore 4.1 software from PANalytical.

X-ray Photoelectron Spectroscopy (XPS) Characterization. Measurements were performed on a Kratos Axix Ultra DLD spectrometer using a monochromatic Al Kα source (15 kV, 20 mA). The photoelectrons were detected at a takeoff angle of $\phi = 0°$ withrespect to the surface normal. The pressure in the analysis chamberwa). Theentained below $7 × 10^{-9}$ Torr for data acquisition. The data wasconverted to VAMAS format and processed using CasaXPS software,version 2.3.17. The binding energy (BE) scale was internallyreferenced to the C 1s peak (BE for C−C = 284.8 eV).

■ RESULTS AND DISCUSSION The synthetic strategy we propose here was inspired by the oneemployed for the nonaqueous synthesis of metal oxide NCs. 52In a typical synthesis of metal oxide NCs, the release of water,i.e., the oxygen precursor, can be achieved by reactingcarboxylic acids with either amines or alcohols at relativelyhigh temperatures (above 200 °C), as illustrated by eqs 1 and 2. Similarly, acyl halides are well known for their strongreactivity toward nucleophilic compounds (i.e., amines,alcohols, carboxylic acids) which form carboxylic acidderivatives even at room temperature (i.e., amides, esters,anhydrides) and simultaneously release hydrohalic acids (see eqs 3−5). 53

$$\text{(1)}$$

$$\text{(2)}$$
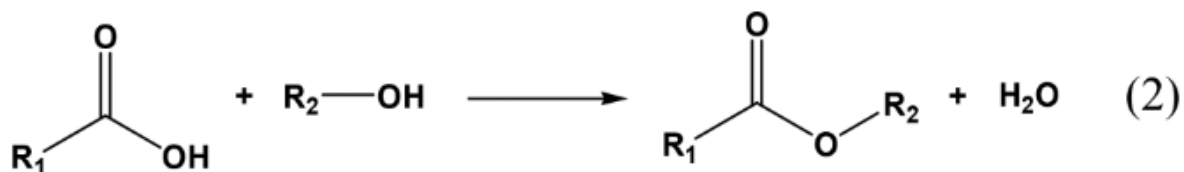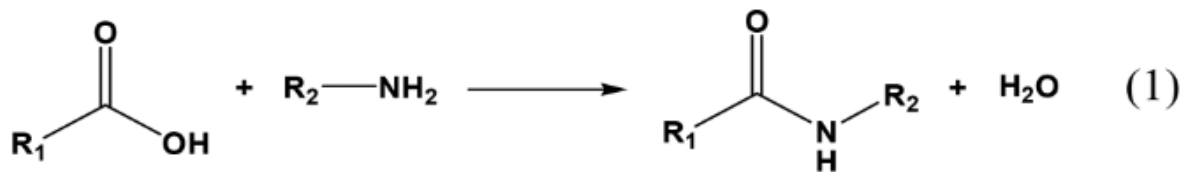
Thus, the idea behind our colloidal approach is to inject acylhalide molecules into a solution of metal cations that have beendissolved in nucleophilic molecules, namely, amines andcarboxylic acids, at a desired temperature, in order to triggerthe release of halide ions and, consequently, the nucleation andgrowth of metal halide NCs. Among the possible acyl

halidemolecules, we selected benzoyl halides since they are low costand have a sufficiently high boiling point (~200 °C), whichallows for the synthesis of metal halide NCs even at relativelyhigh temperatures. Furthermore, considering the strongreactivity of acyl halides toward nucleophilic species, anotherimportant aspect of benzoyl halides is that they are more stablethan aliphatic acyl halides as a result of their stabilization by theπ-overlap in the ground state. 54 Indeed, the more stable theanion precursor is, the more controlled the release of the halideions should be, which, in turn, could lead to the fine tuning ofthe size distribution of the NC. 55In order to understand the efficacy of our synthetic protocol,we tested the synthesis of lead-based halide perovskites NCs,paying particular attention to the optimization of their phasepurity, size distribution, and optical properties. To this end, wechose to synthesize the benzoyl iodide precursor due to thecommercial availability of only the benzoyl chloride andbromide compounds. This precursor can be easily preparedby reacting benzoyl chloride with anhydrous sodium iodide at75 °C in an inert atmosphere (see Experimental Section andFigure S1 of the SI). 51,56First, we will illustrate the results obtained for CsPbX 3 NCs.In a typical synthesis, cesium carbonate and lead acetate weredissolved and degassed in oleylamine, oleic acid, andoctadecene at 130 °C in a three-neck flask. Subsequently, thesolution was heated up to the desired temperature (170−200°C), and the benzoyl halide precursor was swiftly injected intothe reaction flask, triggering the immediate nucleation andgrowth of the NCs (see Experimental Section and Table 1). Bright-field TEM images of CsPbX 3 NCs show that the crystalshad a cubic shape and a narrow size distribution (see Figure1a−c and Figure S2 of the SI). The average size of the CsPbCl 3NCs was 8.6 ± 1.0 nm, while it was 7.8 ± 1.3 nm for theCsPbBr 3 ones and 10.1 ± 1.6 nm for the CsPbI 3 ones.The XRD patterns of CsPbX3 NCs nicely match the cubicperovskite structure (CsPbBr 3 ICSD code 29073, CsPbCl 3ICSD code 23108, CsPbI 3 ICSD code 181288) in all threecases, and no secondary phases were present (see Figure 1d−f).Remarkably, the CsPbX 3 NCs exhibited a narrow PL emissionline width, ranging from 11 (CsPbCl 3), to 18 (CsPbBr 3), to 32nm (CsPbI 3) and had PLQYs as high as 92% (see Figure 1g−i).CsPbCl 3 NCs were of particular interest: while cesium leadchloride perovskite NCs are typically characterized by asignificant nonradiative decay, the PLQY of CsPbCl 3 NCswas measured to be as high as 65%, which is a record value.16,57It is important to highlight that such a high PLQY was observedonly when employing a large excess of the Cl precursor, i.e.,1.8mmol of benzoyl chloride and 0.2 mmol of the Pb precursor(see the Experimental Section). On the other hand, CsPbCl 3NCs were characterized by a weak PL emission when they wereprepared using a lower amount of benzoyl chloride. Forexample, using 0.6 mmol of benzoyl chloride and 0.2 mmol ofthe Pb precursor led to NCs with a PLQY of just a fewpercentage points.Time-correlated single-photon counting (TCSPC) measure-ments that were conducted on APbX 3 NCs revealed, asexpected, that systems with higher band gaps had faster PLdecay rates (see Figure S3a and Table S1 of the SI). 19 Inparticular, the

calculated average lifetimes were 7.7 ns for CsPbCl$_3$ NCs, 12.5 ns for CsPbBr$_3$ NCs, and 21 ns for CsPbI$_3$NCs. The average radiative and nonradiative decay rates that were estimated from the PLQYs and the average PL decay times are reported in Table S1 of the SI. While, in general, lead halide-based perovskite NCs exhibit excellent optical properties, some of these materials are known for their poor structural stability. In particular, red-emitting CsPbI$_3$ NCs, the most interesting materials for photovoltaics applications, suffer from a delayed phase transformation from the metastable cubic (α) phase into the nonluminescent orthorhombic (δ) phase, also known as the "yellow phase".[58] For this reason, different approaches have been reported for the stabilization of the cubic phase, such as the use of alkylphosphonic acids or phosphines in the synthesis of CsPbI$_3$NCs,[47,48] washing procedures employing ethyl acetate,[28] replacing part of Cs+ cations with bigger cations,[44] and replacing Pb^{2+} ions with Mn^{2+} cations.[49,50] In this regard, we observed that the cubic CsPbI$_3$ NCs that were synthesized with our procedure had a high phase stability, without any postsynthesis treatment. The XRD patterns of CsPbI$_3$ NCfilms exposed to air indicated that no phase transition occurred after 20 days (see Figure 2a). Furthermore, our optical characterizations of the NCs after air exposure confirmed the absence of the CsPbI$_3$ yellow phase, since no absorption features appeared at ~440 nm, which can be ascribed to the orthorhombic CsPbI$_3$ band-edge absoption,[59] and the NCs retained their PL emission (see Figure 2b). In order to understand the reason behind the phase stability of CsPbI$_3$ NCs, and possibly also the PL properties of our CsPbX3 NCs, we performed XPS characterization to study their surface and composition. The surface chemistry of lead halide-based perovskite NCs has been shown to play a fundamental role in determining not only their stability in air or under annealing, but also their optical performance.[17,28,60−64] The analysis of the Cs 3d, Pb 4f, and X peaks (Cl 2p, Br 3d, and I3d) revealed that our CsPbX$_3$ NCs were substoichiometric in Cs, while the Pb:X ratio was always close to 3 (see Figure S4 of the SI). In more detail, the Cs:Pb:X ratios found in our NCs were: 0.9:1:3.1 in the case of chlorides, 0.8:1:2.8 in the case of bromides, and 0.8:1:2.7 in the case of iodides. We also roughly estimated the amount of oleylammonium ions bound to CsPbX$_3$ NCs by analyzing the N 1s peak (see Figure S4 of the SI). The chloride and bromide NCs had a ratio of Cs:N close to 1:0.5, and the iodide ones had a ratio of 1:1.2. These results suggest that the surface of our CsPbX$_3$ NCs is lead halide terminated, i.e., the surface Cs ions are replaced by oleylammonium ions. Lead halide perovskite NCs with this type of surface have been reported to have improved stability and enhanced optical properties.[29,63] Indeed, Woo et al. ascribed the improved stability of their CsPbBr$_3$ NCs (which were obtained with the hot-injection method, adding ZnBr$_2$ as an extra bromide source) to their lead bromide-rich surfaces.[29] In addition, Ravi et al. demonstrated that alkylmmonium ions have the ability to substitute Cs ions on the surface of CsPbX3 NCs, which consequently improves their stability and optical properties.[63] We believe that our new synthetic procedure is favorable with regard to the formation of oleylammonium

leadhalide surfaces thanks to the halide-rich conditions that areused (see the Experimental Section). Moreover, the release ofX− ions from the acyl halides is accompanied by theconcomitant release of H + ions, which can drive theprotonation of the oleylamine in solution (see eqs 3−5).As benzoyl halides can be easily mixed together, we alsotested our procedure to synthesize mixed-halide NCs, namely,CsPb(Cl/Br) 3 and CsPb(Br/I) 3. These compounds as well asthe starting CsPbX 3 NCs could be successfully synthesized witha narrow size distribution, phase purity, and good opticalproperties, simply by injecting mixtures of benzoyl halides inappropriate ratios (see Experimental Section and Figure S5 ofthe SI). Also, given the strong reactivity of benzoyl halides evenat room temperature, we tested the CsPbX 3 NCs forpostsynthesis transformations, namely, for anion-exchangereactions. Thus far, the most commonly used precursors foranion-exchange reactions have been metal halide salts (i.e., MX2where M = Pb, Zn, Mg, Cu, Ca and X = Cl, Br, I) andoleylammonium or tetrabutylammonium halides. 20−25 How-ever, a disadvantage of these halide sources is that either theysuffer from poor solubility in nonpolar solvents or theirreactivity is limited at RT. On the contrary, benzoyl halideswere observed to be efficient precursors for anion-exchangereactions: the addition of benzoyl chloride or benzoyl iodide topresynthesized CsPbBr 3 NCs led to a fast blue shift or red shift,respectively, of the peaks in both the PL and the absorptionspectra of the NCs (see Figure 3, Experimental Section, andFigure S6a of the SI). In both cases, the XRD patterns of theresulting NCs confirmed the retention of the parent cubicperovskite structure, and there was a systematic shift of thepeaks induced by the variation of the lattice parameters (seeFigure S6b of the SI). Interestingly, the back-exchangereactions, CsPbCl 3 → CsPbBr 3 and CsPbI 3 → CsPbBr 3, alsoworked efficiently when benzoyl bromide was added to theCsPbCl 3 and CsPBI 3 NC solutions, respectively (see Figure S7of the SI).We then extended our protocol to the colloidal synthesis ofhybrid organic−inorganic APbX 3 (A = MA, FA) perovskiteNCs. We first tested our hot-injection approach by preparingMAPbX 3 NCs which, to date, have been mainly produced usingthe LARP technique since standard hot-injection techniquesresult in NCs with poor optical properties. 32 These hybridorganic−inorganic NCs could be synthesized using theprotocol we devised for CsPbX 3 NCs, with only minormodifications (see Experimental Section). Bright-field TEMimages of representative MAPbX 3 NCs are shown in Figure4a−c. In all three cases, a nearly cubic morphology with anarrow size distribution was observed: the average length of theNCs was 20.1 ± 2.9 nm for MAPbCl 3, 15.5 ± 1.8 nm forMAPbBr 3 , and 8.9 ± 2.4 nm for MAPbI 3 (see Figure 4a−c andFigure S8 of the SI). It is worth mentioning that PbO was usedas the lead precursor for the synthesis of MAPbX 3 NCs insteadof lead acetate as it enabled a better control over the sizedistribution and shape of the final NCs (see the ExperimentalSection and Figure S9 of the SI).According to XRD analysis, the structure of the MAPbBr 3NCs matched the cubic perovskite structure (ICSD code252415) while that of MAPbI 3 NCs exhibited a tetragonalCH 3NH 3 PbI 3 crystal

phase (space group I4/mcm, ICSD code238610). This is in agreement with a recent report by Zhang etal. on identical systems (see Figure 4e and 4f). 38 Given theabsence of any reference pattern for MAPbCl 3 in the ICSDdatabase, we compared the XRD pattern of our MAPbCl 3 NCswith those of bulk crystals that are reported in the literature,and we found a good match with that reported by Maculan etal., which is a cubic perovskite structure (space group Pm-3m)with a = 5.67 Å (see Figure 4d). 65,66The UV−vis absorption and PL spectra of MAPbX 3 NCs areshown in Figure 4g−i. Similar to what has been previouslyreported, all NC samples had a narrow PL emission with afwhm of 15 nm for MAPbCl3, 19 nm for MAPbBr 3, and 43 nmfor MAPbI3 . 15,32,66 Remarkably, the MAPbBr 3 and MAPbI3NCs had a PLQY as high as 92% and 45%, respectively, whilefor MAPbCl 3 NCs the PLQY was around 5%. Similar to thecase of CsPbCl 3 NCs, we did observe an enhancement of thePL emission of MAPbCl3 NCs when increasing the amount ofthe Cl precursor to 1 mmol (see Figure S10a of the SI). Suchimprovement occurred along with the formation of a secondaryundesired PbCl 2 phase (see Figure S10b of the SI). Thesefindings suggest that, as in the case of CsPbX 3 systems, a leadhalide-rich environment could enhance the PL emission of theresulting MAPbCl3 NCs. Unfortunately, in this case suchenvironment leads also to the formation of PbCl 2 which, thus,limits the effective amount of the Cl precursor that can beemployed. Decay lifetimes, which were acquired by means ofTCSPC measurements, were 5.4 ns for MAPbCl3 NCs, 35 nsfor MAPbBr 3 NCs, and 35.7 ns for MAPbI3 NCs (see FigureS3b and Table S1 of the SI).Although the synthesis of MAPbX 3 NCs has been optimizedover the past few years, FAPbX 3 NCs with optimal opticalproperties as well as a narrow size distribution and phase purityhave not yet been prepared by either hot-injection techniquesor by the LARP approach. 18,40,44−46 Lately, these compoundshave received considerable interest since they have severaladvantages over their methylammonium counterparts, such as ahigher stability due to a more symmetric and tightly packedcrystal structure. 67−69 We could also synthesize FAPbX 3 NCsusing our protocol (see Experimental Section). Typical TEMimages of FAPbCl 3 and FAPbBr 3 NCs evidenced a narrow sizedistribution, which became slightly broader in the case ofFAPbI3 NCs (see Figure 5a−c and Figure S11 of the SI). Theaverage size of the NCs was 11.2 ± 1.4 nm for FAPbCl3 , 12.4 ±1.6 nm for FAPbBr 3 , and 14.2 ± 2.8 nm for FAPbI 3. Regardingthe structural analysis, given the absence of any FAPbX 3reference patterns in the ICSD database, we had to comparethe XRD patterns of our FAPbX 3 NCs with those of bulkcrystals which have been recently published. In the case ofFAPbBr 3 and FAPbI3 NCs, a good match was found with thecubic structures reported by Zhumekenov et al. 70 (see Figure5d−f). On the other hand, no cubic bulk structure has beenreported so far for FAPbCl 3 compounds. This can be explainedby its calculated tolerance factor (1.150), which in principle istoo large to allow a 3D phase formation. 71 Conversely, therefinement of the XRD pattern of our FAPbCl3 NCs led to acubic structure (space group Pm-3m) with a = 5.67 Å. Thisrepresents the first report of a cubic FAPbCl3 structure. UV−visand PL spectra of the

FAPbX3 NCs are shown in Figure 5g–i.Furthermore, Br- and I-based compounds exhibited excellentoptical properties and had a high PLQY (92% for FAPbBr 3 and65% for FAPbI3) and narrow PL emission (20 nm for FAPbBr 3and 48 nm for FAPbI3). The FAPbCl 3 NCs were characterizedby having a narrow PL (fwhm = 16 nm) but a low PLQY(about 2%). Decay lifetimes, which were acquired by means ofTCSPC measurements, were 14.8 ns for FAPbCl3 NCs, 30.3 nsfor FAPbBr 3 NCs, and 75.2 ns for FAPbI3 NCs (see Figure S3cand Table S1 of the SI).Finally, we investigated the amplified spontaneous emission(ASE) which occurred in the APbBr 3 NC films. Theseparticular NCs had the highest PLQYs (more than 90% in allthree of cases), much higher than those of their Cl and Icounterparts (APbCl 3 and APbI 3). Figure 6a–c reports theemission spectra showing ASE of the three APbBr3 NC samplestogether with the ASE thresholds. All three systems manifestedvery low ASE thresholds, ranging from 2.2 to 8.1 µJ/cm 2 , whichare either comparable to or lower than the lowest values that have been reported in the literature (see Table S2). 72Moreover, all three of the systems had very narrow ASEfwhm due to the very narrow gain in bandwidth (See FigureS12 of the SI). 73

■ CONCLUSIONS We have demonstrated a new colloidal route for thepreparation of both all-inorganic and hybrid organic–inorganicAPbX 3 NCs (A = Cs, MA, FA and X = Cl, Br, I). Our approachis based on the injection of benzoyl halides (as halideprecursors) into a solution of desired cations and properligands (oleylamine and oleic acid) at a desired temperature.After the injection, a fast release of halide ions occurs, which isfollowed by the nucleation and growth of metal halide NCs. Inall cases, the resulting APbX 3 NCs show a high phase stability, avery good size distribution, and excellent optical properties.They exhibit a narrow PL emission and high PLQYs, which arearound 90% in the case of APbBr3 systems, 55% in the case ofAPbI3 materials, and a record value of 65% in the case ifCsPbCl 3 NCs. The optical quality of our materials was alsoreflected by the low values of their ASE thresholds. The originof such improvements with regard to the stability and opticalproperties of CsPbX3 NCs was tentatively ascribed to theformation of lead halide-terminated surfaces in which Cs ionsare partially replaced by oleylammonium ions. Indeed, theformation of such surfaces is promoted by our syntheticconditions. To conclude, we believe that the versatility of oursynthetic approach will allow for the future development of all-inorganic and organic–inorganic lead-free metal halide NC systems.

■ ASSOCIATED CONTENT*S Supporting InformationThe Supporting Information is available free of charge on theACS Publications website at DOI: 10.1021/jacs.7b13477.NMR characterization of benzoyl iodide, size distributionof all of the APbX 3 NCs, time-resolved spectroscopiccharacterization, control experiments on MAPbCl 3 NCs,XPS analysis, CsPb(Br/I) 3 , and CsPb(Cl/Br) 3 NCs,anion-exchange results, MAPbBr 3 NCs synthesized withlead acetate trihydrate, overview of reported ASEthresholds (PDF)

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