Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals

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Abstract. Lead halide perovskites (LHPs) in the form of nanometer-sized colloidal crystals (nanocrystals, NCs) have attracted the attention of diverse materials scientists due to their unique optical versatility, high photoluminescence quantum yields and facile synthesis. LHP NCs have a “soft” and predominantly ionic lattice, and their optical and electronic properties are highly tolerant to structural defects and surface states. Therefore, they cannot be approached with the same experimental mindset and theoretical framework as conventional semiconductor NCs. In this review, we discuss LHP NCs historical and current research pursuits, challenges in applications, and the related present and future mitigation strategies explored.

One way of introducing lead halide perovskites nanocrystals (LHP NCs) is to place them in the context of research on colloidal semiconductor NCs, which started several decades ago and that is still flourishing. A historical account on LHP NCs research, beginning from early studies on metal halides, is reported in Box 1. The next section will give a snapshot of the main structural features of LHP NCs and their synthesis approaches. The challenges related to the stability of LHP NCs and possible strategies to address this issue will be discussed in the subsequent sections. Finally, prospects for applications in consumer optoelectronics, as well as in single-photon sources will be provided. For other aspects of colloidal LHP NCs, we refer the reader to several recent reviews.¹⁻³

Soft ionic crystal structure and facile synthesis of LHP NCs

Traditional colloidal semiconductor NCs, which have been actively investigated since the discovery of the hot-injection, high-temperature synthesis of Cd chalcogenide NCs,⁴ primarily constitute binary compounds with rather simple crystal structure types: tetrahedrally-bonded compounds of zinc-blende (chalcogenides: ZnS, ZnSe, CdS, CdSe, HgTe; pnictides: InP, InAs) or wurtzite (ZnS, ZnSe, CdS, CdSe) structure, or face-centered rock-salt-type compounds (PbS, PbSe). In this review, those semiconductor NCs which are spheres or cubes smaller than 20 nm and are therefore quantum-confined in all three dimensions, are also termed quantum dots (QDs). The anions and cations in the crystals of these traditional semiconductor NCs have crystallographically identical positions/sublattices. LHPs (Fig. 1a) instead crystallize in the cubic APbX_3 -type perovskite lattice [where A is methylammonium (MA, CH_3NH_3^+), formamidinium (FA, $\text{CH}(\text{NH}_2)_2^+$) or cesium (Cs^+), X is one or more halides (Cl^- , Br^- or I^-)] or its octahedrally tilted variants, isostructural to traditional oxide perovskites such as CaTiO_3 . These structures are characterized by the 3-dimensional (3D) interconnection of their $[\text{PbX}_6]^{4-}$ octahedra, with the A-site cation residing in the large voids in between. The typically cubic or orthorhombic symmetries of these lattices are apparent in the commonplace observation of the cuboidal shapes of the LHP NCs (Fig. 1b). According to the Goldschmidt tolerance factor, which concerns the close-packing of ions, only MA, FA and Cs ions can stabilize the 3D PbX_6 framework due to their geometric fitness within a twelve-coordinate A-site. Larger or smaller cations favor the formation of polymorphs of a lower dimensionality (0D, 1D or 2D),

with edge- or face-sharing of the octahedra, and as a consequence, larger and often indirect energy bandgaps.⁵ For a more detailed account of the peculiarities of the crystal chemistry of divalent metal perovskites, we direct the reader to a recent review article.⁶ Here we emphasize that unlike the oxide perovskites, LHPs exhibit much lower melting points (400-500 °C in CsPbX₃) due to lower ionic charges and larger interatomic distances, as well as a higher propensity to thermal decomposition (below 300 °C for MA- and FA-based materials).

The chemical bonding in LHPs is intrinsically much more ionic than in the more rigid, highly covalent lattices of metal chalcogenides and pnictides. This has broad implications for the synthesis, surface functionalization and processing of LHP NCs. Conventional QDs require elevated synthesis temperatures in order to promote crystallization. Existing hot-injection synthesis methods, typically at temperatures of 100-350 °C, are ideal for NCs of moderately ionic compounds such as Cd and Pb chalcogenides, and to a large extent also for InP QDs. However, it remains challenging to synthesize high-quality Si and GaAs QDs in the standard solution phase fashion, even at temperatures as high as 400 °C.⁷ Their synthesis also requires molecular precursors that are highly air-, moisture- or heat-sensitive or difficult to make. In contrast, due to their highly ionic bonding, LHP NCs form within seconds even at room-temperature (RT), from a vast selection of precursors.⁸⁻¹⁰ Initially, the synthesis and processing of CsPbX₃ NCs were primarily approached with the same methods as conventional QDs. For example, ligand-assisted hot-injection synthesis (RT-200 °C) was used to synthesize the first CsPbX₃ NCs.⁹ An alternative strategy is the ligand-assisted re-precipitation method, wherein an ionic solution of the respective ions (A⁺, Pb²⁺ and X⁻) in a polar solvent is rapidly destabilized by mixing with a non-solvent inducing a burst of nucleation, as originally proposed for MAPbBr₃ NCs.⁸ Both methods are applicable to the whole APbX₃ family and the reaction conditions can be adjusted to yield non-cuboidal shapes, such as nanoplatelets, nanosheets and nanowires.^{2, 11-13} Other facile routes to colloidal LHPs include microwave-assisted synthesis, sonication of the precursors in a solvent/ligand mixture and ball-milling.¹⁴⁻¹⁶ Automated, high-throughput screening, such as using robotics¹⁷ or microfluidics equipped with on-line optical characterization,¹⁸ can also enable accelerated progress in the discovery of novel perovskite NCs.

The major practical challenges facing LHP NCs are related to their highly labile structure, as discussed in detail in a dedicated section of this review. Nanoplatelets, nanosheets and

nanowires are typically fully stable in their crude solution after synthesis, but eventually convert to cuboidal or other irregular shapes, or recrystallize into the bulk material upon isolation and purification, upon concentration or dilution, or under strong UV irradiation. In the case of nanowires, satisfactory durability is found only in wires with a diameter of 10-200 nm. Thus far, the synthesis of stable, few-nm sized QDs or atomically-sized clusters has remained elusive for LHPs. Sub-5 nm quantum-confined LHP NCs could be produced, but only via non-colloidal approaches, by the ligand-free, templated growth of LHP in ordered mesoporous silica scaffolds.^{19, 20}

Figure 1. Colloidal lead halide perovskite nanocrystals. (a) The APbX₃ perovskite structure with 3D-corner-sharing octahedra. Two typical structures are shown: cubic (MAPbX₃, FAPbX₃; two unit cells shown) on the left and orthorhombic (CsPbX₃) on the right; (b) high-angle annular dark-field scanning transmission electron micrograph (HAADF-STEM) of a single, cube-shaped CsPbBr₃ NC, with 15 nm edge length; (c) photograph of highly luminescent colloidal LHP NCs (from left to right, CsPbBr₃ with emission peak at 520nm, CsPb(Cl/Br)₃ emitting at 450 nm and FAPb(Br/I)₃ emitting at 640nm). Figure (c) is courtesy of Dr. Yevhen Shynkarenko.

Defect tolerance

Conventional wisdom, developed over decades of research on Si, CdTe, GaAs and other conventional semiconductors, holds that PV-grade electronic quality requires ultralow concentrations of impurities and crystalline defects, typically at ppb-levels, that all act as dopants or electronic traps. LHPs are different, as highly efficient LHP PV devices can be easily fabricated based on polycrystalline films synthesized with technical-purity chemicals at low temperatures, deposited in an ambient atmosphere and, often, containing an ultra-high density of point defects such as vacancies (up to 1-2 atomic %). Likewise, LHP NCs are bright

emitters without electronic surface passivation. It is clear that the electronic properties of LHPs are highly tolerant to the material's defects and surfaces.²¹ This defect tolerance seems to be a fortunate coincidence of several factors. Firstly, out of a large variety of conceivable point defects, only vacancies (primarily A- and X-site vacancies, Fig. 2a) are characterized by sufficiently low formation energies and are therefore exclusively observed. Interstitial and anti-site defects, which would form deep trap states in the electronic structure, are almost absent^{22, 23} since ions in the perovskite lattice are energetically difficult to misplace. Secondly, the shallow character of the vacancy-related states is due to unique specifics of the bonding in LHPs, namely the antibonding character of the valence band maxima (with mixed I 5p and Pb 6s character; Fig. 2b) and spin-orbit effects in the conduction band (which has a predominant Pb 6p character). NC surfaces can simply be imagined as a plane of vacancies and should therefore exhibit similarly benign behavior as vacancies. This intuition explains the observation of high PL QYs without surface passivation in LHP NCs. However, it should be also pointed that LHP NCs are not entirely defect-free, as PL QYs are normally reported in the range of 80-95% in the green-red region and down to 10-20% at the blue border region (close to 400 nm, i.e., CsPbCl₃). Yet, these values greatly exceed any other non-passivated QD material in the same range of wavelengths. There exist multiple reports of the beneficial effects of various post-synthetic ligand treatments, such as with thiocyanates, PbBr₂ or trioctylphosphine-PbI₂, raising the PL QY close to 100%,^{24, 25} presumably due to the improved passivation of under-coordinated Pb ions. Thirdly, the soft and dynamic nature of the perovskite lattice is such that this material has been defined a "crystalline liquid", to highlight the simultaneous emergence of its crystalline and liquid-like properties. These features seem to protect its carriers from trapping and scattering.²⁶ Together with its partial ionic character, the intense structural dynamics of PbX lattices at RT leads to the coupling of electrons and holes with ionic displacements or, in other words, the formation of polarons (Fig. 2c). These polarons have been proposed to screen the Coulombic potential and reduce trapping and carrier scattering, both mutually and with charged defects and optical phonons.^{26, 27} In hybrid perovskites, the A-site molecular rotational motion on the (sub-) ps timescale also allows for the screening of hot carriers,^{26, 27} which potentially creates the possibility of harnessing the hot-carrier energy in order to improve the efficiency of solar cells or to observe hot-carrier PL.

The defect tolerance of LHPs, emerging from the s and p contributions of the Pb atoms, is also pronounced in Pb chalcogenide NCs, which exhibit bright PL without surface

modification except when oxidized. The far greater complexity of the defect formation in Pb chalcogenide NCs has been recently summarized,²⁸ pointing out the importance of the dielectric constant, effective masses and defect-defect interactions in these mechanisms. Interestingly, the role of defect-defect interactions might be engineerable by external impurities. Overall, a unified understanding of the exceptional defect-tolerance in LHPs has not been achieved at the current time.

Figure 2. Factors contributing to the defect-tolerant behavior of LHPs. Overall, the defect-tolerance in perovskite NCs emerges from three distinctive features: their crystal structure, favoring the formation of vacancies but no other point defects; their peculiar electronic structure that makes vacancies benign; and their dynamic lattice effects such as formation of polarons, thereby preventing carriers from trapping. (a) Typical point defects in LHPs, including vacancies, interstitial and anti-site atoms, in order of increasing formation energy (or decreasing probability of occurrence), and their depths in the bandgap. (b) Schematic representation of electronic band structure of typical defect-intolerant semiconductors and LHPs. In conventional semiconductors, such as cadmium chalcogenides, the bandgap is formed between bonding (σ) and antibonding (σ^*) orbitals. Point defects or dangling bonds emerge as weak bonding or non-bonding states within the bandgap. In LHPs, the bandgap is formed between two anti-bonding orbitals. Defects states will thus form only shallow traps or will be enclosed in the conduction or valance band, and will thus not strongly influence the radiative recombination and other optical properties. (c) Schematic representation of local structural deformation of the Pb-Br framework that, combined with a charge carrier (electron or hole), forms a polaron.

Structural lability and how to handle it

Structural and optical stability will remain as the foremost challenge for LHP NCs in the research spotlight. An important paradigm about LHP NCs is that, as easy as it is to make them, it is just as easy to break them. Hence, the retention of their colloidal and structural integrity during isolation, purification and handling has been a problem of paramount importance. The ligand chemistries of conventional QDs have so far primarily relied on

long-alkyl-chain ligands bound to the NC surface via a single anchoring group,²⁹ or on carboxylate or phosphonate (X-type) ligands attached at surface metal adatoms.^{29, 30} LHP NCs are terminated by oleylammonium bromide and/or oleylammonium carboxylate.³⁰ Each of these coordinates to the surface as an ionic pair: ammonium groups displace a surface A-site cation, whereas carboxylates (bromides) act as surface anions. These ligands tend to quickly desorb (Fig. 3a).³⁰ The most dramatic consequence of such loose ligand binding is the difficulty met in isolating and purifying colloids using standard methods for QDs, namely by a repetitive precipitation with a non-solvent followed by redispersion in a pure solvent. More static surface coordination might be expected from the ligands containing several anchoring groups, such as zwitterionic molecules (Fig. 3b), containing quaternary ammonium and carboxylate groups (or sulfonate, phosphonate, or other groups). Oligomeric ligands with a larger number of these charged groups and long hydrocarbon chains per molecule can be envisaged as well.

The fairly ionic bonding character and low crystal lattice energy render LHPs somewhat soluble in nearly all polar organic solvents; in practice, this eventually disintegrates LHP NCs upon exposure to such solvents. This problem will remain difficult to mitigate until a strategy for the full encapsulation of individual LHP NCs in an inert shell is identified (for instance, within silica, titania, alumina, salts with extremely low solubility products such as BaSO₄ or similar, see Fig. 3c). A classical approach to coating LHP NCs with SiO₂, however, would require adapting a sol-gel process such as the Stöber method. This has not been demonstrated yet, presumably due to the necessity of using alcohols or similar protic polar solvents. As a result of LHP NCs being so fragile, complex morphologies, such as core-shell NCs and other NC heterostructures, have not been demonstrated to this date.

Intrinsic chemical instability remains the major issue concerning MA-based LHPs and, to a far lesser but still significant extent, FAPbX₃. MA-based LHP compounds have a low energy of formation and even decompose at RT. This decomposition is reportedly accelerated by heat, light, moisture and oxygen, as well as by the high surface area of the NCs, yielding PbX₂ and several volatile products (CH₃NH₂, HI, I₂ and other species). Thus, future applications are foreseen to be primarily limited to FA- and Cs-based LHP NCs. Poor thermal stability is another major challenge for nearly all future applications of LHP NCs. Hybrid organic-inorganic LHPs decompose before melting (MAPbI₃ at ca. 150-200 °C;

FAPbI₃ at *ca.* 290-300 °C), while the melting points of fully inorganic LHPs are slightly higher (450-500 °C for CsPbBr₃ and CsPbI₃). LHP NCs are all highly prone to sintering. This poses a great challenge for any device architecture relying on the retention of quantum-confined states in a densely packed array of LHP NCs or for devices operating at elevated temperatures, such as lasers or remote phosphors.

Another form of structural lability is observed in red-emitting CsPbI₃ (both in the bulk and in NCs). In this case, the Cs⁺ ions are too small to be included in a 3D perovskite Pb-iodide cage, causing the transition to another polymorph of a lower dimensionality and, hence, a much wider bandgap.^{31, 32} It has, on the other hand, also often been reported that a variation in the purification procedure and the exclusion of air during handling and storage do extend the lifetime of metastable 3D-CsPbI₃ phases.³³⁻³⁵ Considerable work has been done, both with NCs and thin films, to stabilize CsPbI₃ by partially replacing Cs⁺ with larger cations (the foremost example being FA⁺), and by partially replacing I⁻ with Br⁻.^{34, 36} A similar stabilization effect was reported for the replacement of Pb²⁺ with smaller cations such as Mn²⁺ and Bi³⁺, as shown by a retention of bright red PL.³⁷⁻³⁹

Beyond solution-phase chemistry, another underestimated opportunity might deserve further attention, especially in the context of the thermal and environmental stabilization of LHPs. Dynamic structural disorder on fs-ps timescales suggests that it might be very difficult if not impossible to coat LHP NCs with crystalline shells with interfaces that are structurally stable. A promising alternative path to stable LHP emitters is the melt-growth of glass-embedded LHP NCs (Figure 3d), such as in recent reports employing typical phosphate or borosilicate glasses.⁴⁰⁻⁴³ Thus-obtained crystalline NCs, whose size is tunable by melt-quenching and by adjusting the subsequent thermal conditions, are surrounded by an amorphous, chemically stable, water- and oxygen-impermeable glass matrix. Such glass-embedded NCs, easily obtainable in powdered form by a grinding step after quenching the melt, can be easily integrated into any down-conversion-based application of LHP emitters – be it backlighting in displays or as a remote phosphor in lighting.

Figure 3. Structural lability of lead halide based perovskite NCs, and stabilization methods. (a) LHP NCs often lose their colloidal stability, or even structural integrity, due to the desorption of weakly bound ligands. Viable strategies for attaining stable surface coverage by ligands include (b) using zwitterionic long-chain molecules; (c) overcoating with dielectric shells or compositionally matched salts; and (d) matrix-encapsulation into polymers with low water and oxygen transmission rates or crystalline and amorphous inorganic matrixes.

From labile LHP NCs to nanocrystal transformers

The high ionicity and structural instability of LHP NCs can also be exploited for post-synthetic transformations, either with the retention of the original crystal structure, or through reorganization into a new crystal structure. In well-controlled cases, such transformations take place while preserving the overall NC size and shape, or at least the initial size uniformity, as depicted in Figure 4.^{34, 44-47} Perhaps the most striking example is that of anion exchange,^{44, 45} whose fast rate can be attributed to the high concentration of halide vacancies and the high mobility of singly charged halide anions. The PL color of LHP NCs can be adjusted by anion-exchange to any wavelength in the visible spectrum, starting from just one progenitor NC sample (Fig. 4a). It has further been established that mixed-halide compositions in NCs are more easily retained than in thin-films, which suffer from photo-induced halide-ion segregation.⁴⁸ In metal chalcogenide NCs, only the cations have been manipulated in a similarly facile way.⁴⁹ In LHPs, the high plasticity of the lattice enables the exchange of both cations and anions. The A-site cations can be partially or fully exchanged (Cs^+ with FA^+ or MA^+ , and in reverse),³⁴ whereas Pb^{2+} can be partially exchanged with Sn^{2+} , Cd^{2+} and Zn^{2+} cations (Fig. 4b,c).⁴⁷ Similarly, doping CsPbCl_3 NCs with several at%

of Mn^{2+} yields strongly orange-luminescent NCs (PL QY = 58%; emission from the dopant).^{50, 51} Extensive restructuring of LHP NCs is also possible, by either eliminating or adding ions (Fig. 4d-g). For instance, upon removing $\frac{3}{4}$ of the Pb atoms in the form of PbX_2 , CsPbX_3 NCs can transform into Cs_4PbX_6 NCs,⁵² which are characterized by a structure in which all $[\text{PbX}_6]^{4-}$ octahedra are disconnected from each other (oD-perovskite). Back conversion into CsPbX_3 NCs can be accomplished by re-inserting PbX_2 into Cs_4PbX_6 NCs or by extracting CsX by the action of suitable ligands.^{46, 53, 54} It is also possible to extract PbBr_2 from CsPbBr_3 NCs, forming CsBr NCs or, *vice versa*, to convert pre-synthesized CsBr NCs into CsPbX_3 NCs. These conversions are readily observable owing to a color change due to the large difference in bandgap energies (2.43 eV for CsPbBr_3 , 3.95 eV for Cs_4PbBr_6 and 7.3 eV for CsBr). Such chemical transformations, using a presently unexplored variety of A- and B-site metals, will enable the discovery of new functional metal halide NCs, including those that cannot be obtained by direct synthesis.

Figure 4. Structural and compositional post-synthetic engineering of lead halide perovskites. (a) Anion exchange enables bandgap tuning over the whole visible spectrum,

as shown in the left inset. (b) “B” cation exchange allows the study of the optical properties of other divalent metals, such as Mn^{2+} (whose photoluminescence at various concentrations is shown in the right inset) in an LHP environment. (c) “A” cation exchange allows the tuning of the thermodynamic stability (left inset) of the 3D-LHPs by mixing Cs^+ with, for instance, FA^+ , which is key to the stability of iodides. (d) Phase-transformation from CsPbX_3 to Cs_4PbX_6 and CsX via reactions with Pb^{2+} or PbX_2 . (e-g) TEM images of NCs obtained by deliberate transformations between different Cs-Pb-Br compounds.

LHP NCs vs. conventional QDs. A comparison between the physical and electronic properties of conventional QDs and LHP NCs is shown in Table 1. For decades, the primary challenge facing semiconductor NCs was the suppression of the role of mid-gap surface traps that render practically all as-synthesized semiconductor NCs that emit in the visible range poorly luminescent. This has been conventionally mitigated by the elaborate synthesis of sophisticated, core-shell CdSe-CdZnS NCs, via decoupling of the excitonic recombination from surface states. These NCs feature high PL QYs of up to 95-100%, narrow emission lines and excellent long-term stability, and they are currently applied as down-converting materials in several brands of modern liquid-crystal television displays (LCD-TVs) with high color saturation. From the first reports on, unpassivated LHP NCs have exhibited high PL QYs even when the synthesis was performed under ambient conditions and/or without pre-purified chemicals. Small FWHM and high PL QYs are also repeatedly reported with more complex, mixed-cation Cs/FA and mixed halide (Cl/Br, Br/I) stoichiometries.³⁴ Solution-based compositional engineering has shown to be possible on all three lattice sites within LHPs, such as in $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ or $(\text{Cs/Rb/FA/MA})\text{Pb}(\text{Br/I})_3$.^{55, 56} However, it is difficult to achieve a combination of high optoelectronic quality and atomistic homogeneity in multinary metal chalcogenide NCs (CuInS_2 , $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ and $\text{Cu}_2\text{ZnSnS}_4$)⁵⁷ and it remains completely elusive for pnictide NCs. Typically, for the tetrahedrally-bonded compounds, site disorder (interstitial and anti-site atoms) and phase inhomogeneities are enhanced in NCs as compared to the bulk. In contrast, the LHP lattice, wherein ions cannot easily be misplaced due to their specific sizes, coordination numbers and ionic charges, is intrinsically immune to such defects. With regards to multinary LHP NCs such as $(\text{Cs/FA})\text{Pb}(\text{Br/I})_3$, a detailed structural analysis is still pending and will be crucial for further taming the presently unstable red and near-IR emitting LHP NCs.

Table 1. Comparison of the chemistry, durability and optical performance of LHP NCs with conventional NCs. Only NCs emissive in the visible spectral range are included.

	<p>Metal chalcogenide (II-VI) and pnictide (InP) core-only nanocrystals</p>	<p>Metal chalcogenide and pnictide core/shell nanocrystals</p>	<p>Lead halide perovskite nanocrystals</p>
Crystal structure	wurtzite, zinc-blende	wurtzite, zinc-blende	perovskite
Composition	CdSe, ZnSe, InP	CdSe/CdS, CdSe/CdZnS, InP/ZnS	(Cs,FA)PbX ₃ (X=Cl, Br, I), homogeneous, multinary compositions possible
Used in	no commercial use	LCD TV (Samsung, Sony, <i>etc.</i>), discontinued for Cd-based.	under development for LCD TV
Spectral range and efficiency	entire visible (400-700 nm) for II-VI and limited for InP (520-700 nm)	limited (510 - 650 nm)	entire visible (400-700 nm)
PL QY	low (0-10%)	high (up to 95%)	high (up to 99+%)
FWHM	narrow for II-VI (<25 nm; e.g. <100 meV), but limited for InP-based (<i>ca.</i> 40 nm at 530 nm PL peak)		narrow over entire visible range (<100 meV)
Defectiveness	low in binary compounds; high in multinary compositions (vacancies, antisites and interstitials)		intrinsically high (vacancies)
Synthesis	high-purity precursors and rigorous air-free synthesis; high-temperature	elaborate, lengthy synthesis; high-temperatures	facile synthesis; possible under ambient conditions
Post-synthesis tunability	only cation exchange		cation exchange (both A and B sites) and anion exchange
Surface ligands	highly versatile organic and inorganic surface functionalization		limited affinity to the surfaces; new ligand chemistries are urgently needed
Heteronanostructures	yes (complex core shells/dumbbells/Janus <i>etc.</i>)		none to date
Thermal stability	stable	stable	limited to below 100 °C due to low melting points
Oxidative and photostability	low to moderate	high	high
Solvent compatibility	compatible with all solvents, including water		finite solubility in water and many polar solvents, insoluble in all others
RoHS compliance	limited for CdSe-based (100 ppm limit for Cd), unlimited for InP-based		limited but higher than for CdSe-based (1000 ppm limit for Pb)
Single-dot PL			
Single-photon emission	yes	yes	yes
Multi-exciton	low yield	high yield	high yield

emission			
Blinking	yes	reduced	reduced
Photobleaching	fast	moderate	moderate
Emission rate	~10 ns (RT), sub- μ s (5K)	10-100 ns (RT), sub- μ s (5K)	1-50 ns, longer for iodides (RT), sub-ns (5K)

Consumer optoelectronic devices with LHP NCs

The wide color gamut of the PL of LHP NCs meets the existing color standards for display applications (Figure 5a). The small FWHM of this PL of ≤ 100 meV corresponds to just 18-20 nm in the green region around 520-530 nm (CsPbBr₃, FAPbBr₃ NCs), making such emitters valid contenders with traditional green phosphors. A promising near-future application for LHP NCs is therefore in LCD backlighting, for which color-pure green and red emitters with PL peaks centered at 530 nm and 630 nm are desired. Closely related prospective applications include remote phosphors for lighting and color-controlling and color-enhancing films in portable gadgets. The InP-based NCs currently used in Samsung SUHD TV displays have broader PL bands (FWHM ≈ 40 nm at 530 nm), which are difficult to improve upon due to inherent compositional and morphological inhomogeneities in the few-nm-sized InP-based emissive cores. Towards display applications, the incorporation of LHP NCs into optically transparent polymers or into an inorganic matrix is an obvious strategy for thermal and environmental stabilization. Encouraging results on the long-term stability of such emitters were indeed obtained by incorporating LHP NCs in water-nonpermeable polymers and into salt matrixes (potassium halides or Cs₄PbX₆).⁵⁸⁻⁶⁰

The fact that electronic surface passivation with wide-gap shell materials is not required for LHP NCs might be a decisive advantage for facile charge carrier injection in light-emitting diodes (LEDs). Thus far, LEDs based on CsPbBr₃ NCs are the most studied, with typical external quantum efficiencies (EQEs) of 6.3%⁶¹ and 8.7%⁶². The former study reported a peak luminance of over 15'000 cd/m², while the latter reported a more modest value of 1'660 cd/m². Both studies highlight the importance of purifying LHP NCs from excess ligands. Red CsPbI₃ NC LEDs showed an EQE of 7.3% and a peak luminance of 435 cd/m² at 688 nm.⁶³ It remains difficult to construct efficient blue LEDs with perovskite NCs, where the best example is that of MAPbBr_{1.5}Cl_{1.5} NCs,⁶⁴ which exhibit an EQE of 1.18% and a peak luminance of 2473 cd/m² at

445 nm. For the blue-most CsPbCl₃ NCs, the highest achieved EQE to date is only 0.61% and the corresponding luminance was 11 cd/m² (at 404 nm).⁶³

LHP NCs also show great promise as versatile solution-based precursors for the low-temperature fabrication of absorber layers for PV (Figure 5b).⁶⁵ Solar cells with efficiencies up to 10.8% were demonstrated using CsPbI₃ NC thin-films deposited by multiple rounds of sequential spin-coating and ligand-removal steps.³³ We expect further progress in this direction, utilizing more complex compositions of LHP NCs. This is motivated by recent trends in thin-film LHP PV where power conversion efficiencies exceeding 20% have been reported, by employing mixed-cation and mixed-anion compositions such as (Cs/Rb/FA/MA)Pb(Br/I)₃.⁵⁶ NC-based synthesis routes to such complex thin-films might have certain inherent advantages. For example, although the deposition of such films requires the solubilisation of all of the precursor salts in polar solvents, coating, annealing and recrystallization of the LHPs in a single step, the use of LHP NCs separates the mixing of ions, film-formation and crystallization into three different steps. The nonpolar solvents used for depositing NCs might also be advantageous, for example, in maintaining solvent orthogonality in the deposition from solution of consecutive layers of the device. LHP NCs are also unique in their ability to form bulk heterojunctions with other solution-processable materials such as conductive polymers, fullerenes or other QDs.

Figure 5. Optoelectronic applications of LHP NCs. Owing to high PL QYs, narrow FWHM and tunability over the entire visible spectral range, LHP NCs can find applications in PL down-conversion (a, LCD displays and lighting), in electroluminescent devices (b, LEDs) and in solar cells (c).

Toxicity of lead and exploration of lead-free LHP NCs

The presence of lead in LHPs raises obvious concerns about the toxicity of these materials upon introduction into consumer electronics. One should note here that the industrialized world has been exposed to massive amounts of lead over the decades. A now infamous, volatile compound, tetraethyl lead, has been used since the 1920s as an additive to fuels, and although its phasing out from automotive applications began in the 1970s, it is still far from completion. In its non-volatile, metallic form, or as stable and insoluble solid compounds, Pb remains widely used in, for example, lead-acid batteries, solder in silicon solar cells, piezoelectrics and even as a white pigment (PbO_2).

The European “Restriction of Hazardous Substances” (RoHS) directive limits the use of heavy-metal-based substances in electrical and electronic equipment. The current limit for lead is 1000 ppm by weight in any continuous solid component of the device, which is not as stringent as the current limit for cadmium (100 ppm by weight). Current Cd-based QD TV displays require only about 1.5 mg of Cd (for a 55 inch display).⁶⁶ For LHPs, one could assume that roughly the same quantity of Pb would be needed based on nearly identical extinction coefficients in blue (450-470nm; GaN emission for excitation) and similarly high PL efficiencies at the same PL wavelengths (530 and 630 nm). This corresponds to sub-1000 ppm concentrations of Pb within the 50-100 μm thick polymer film, hence not requiring an RoHS exemption. With regard to consumer electronics, the recycling policies for Pb are well detailed and are highly efficient.

Efforts are underway to find environmentally benign and, at the same time, chemically robust alternatives to lead-based chemistries for optoelectronic applications. As discussed above, defect-tolerant semiconductors are those in which both the s and p electrons of a metal hybridize to form the valence and conduction bands. In accordance with this principle, Sn^{2+} and Ge^{2+} analogues of LHPs do exhibit bright emissions but, unfortunately, are highly unstable. Even trace oxygen quantities cause degenerative p-type doping in tin and germanium perovskites through oxidation. Furthermore, Sn-based analogues of LHPs are, from a toxicity point of view, not ideal alternatives.⁶⁷ High stability and bright emission have been reported for oD-perovskite-like structures $(\text{C}_4\text{N}_2\text{H}_{14}\text{Br})_4\text{SnX}_6$ (X = Br, I),⁶⁸ but with a very large FWHM of above 100 nm at RT.

The solar cell community has contributed great effort in the search for lead-free, LHP-like semiconductors.⁶⁹ In particular, the replacement of Pb^{2+} with oxidatively stable Bi^{3+} is an

attractive option. However, such ternary halides are structurally very different from LHPs since they typically crystallize into 0D or 2D networks of M-X polyhedra, usually with indirect band gaps, such as in $\text{Cs}_3\text{M}_2\text{X}_9$ ($\text{M} = \text{Sb, Bi, In}$).⁷⁰ So far, these phases have not exhibited efficient PL at RT. To retain the 3D-interconnection of octahedra, double perovskite compositions of $\text{A}_2\text{M}^{1+}\text{M}^{3+}\text{X}_6$ have been investigated, such as $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{AgInCl}_6$.^{71, 72} Such compounds have not yet shown photophysical characteristics on par with LHPs, and they exhibit indirect band gaps, making them unsuitable as emitters.

Overall, despite the growing skepticism of the PV community about the near-term probability of finding a substitute for LHPs amongst its close structural and compositional analogues, the chances of developing bright, LHP-like nanoscale emitters are, in our opinion, far greater. The reasons for this optimism are as follows. First, while PV materials must have bandgaps beyond 700 nm, LHP NCs as bright emitters are primarily needed to function with bandgaps of 450-700 nm. Hence, many materials discarded by the PV research community might be perfectly suited for constructing NC emitters. Second, the spatial confinement of carriers in NCs usually drastically enhances the PL QY. To this end, and in retrospect, the bright green PL from CsPbBr_3 could have been discovered much earlier; this compound has been known for over 100 years, and all that was needed to be done was intense mechanical grinding of the bulk material. However, this idea would have been hard to conceive of since bulk CsPbBr_3 is essentially non-luminescent. In conclusion, it seems to make quite some sense to revisit numerous compounds that were discarded as PV materials and to systematically synthesize them in nanoscale form in order to observe whether or not they become luminescent.

Figure 6. LHP NCs as single-photon sources. (a) Typical ensemble absorption and PL spectra from CsPbBr₂Cl NCs recorded at RT, an ensemble PL spectrum recorded at T = 5 K and three representative single-dot spectra. (b) Time series of PL from a single CsPbBr₂Cl NC at 6 K, showing stable emission without blinking and with minimal spectral diffusion. (c) Representative single-dot spectra from CsPbX₃ NCs of various compositions. (d) Time-resolved PL traces for NCs of various compositions. (e) Polarization dependent single CsPbBr₂Cl NC PL spectrum. The inset (top-right) shows the polarization of each of the spectral features. In this case, three linearly polarized PL peaks are observed. Schematics (top-left) of the band-edge excitonic states in CsPbX₃ NCs comprising a three-fold split bright triplet state and a dark singlet state. (f) Future LEDs featuring individually addressable single NC emitters. Figures (a & b) are adapted with permission from Ref.⁷³

Figure (c), courtesy of IBM Research – Zurich (M. A. Becker, T. Stöferle, R. F. Mahrt). Figures (d & e) are adapted with modifications from Ref.⁷⁴

LHP NCs as single-photon sources

In addition to conventional optoelectronic devices, colloidal semiconductor NCs can be employed as non-classical light sources (single photon emitters)⁷⁵ that might play a pivotal role in future quantum technologies (such as quantum cryptography, quantum sensing and quantum communication).⁷⁶ At this time, most such studies have concerned CdSe-based NCs. The common challenges of such applications, including emission intermittency (blinking), photo-instability and spectral diffusion, originate from factors that are inherent to the QD material (for instance, surface traps, enhanced Auger processes, facile photoionization, photo-oxidation and other environmental effects).⁷⁵ Specially designed core-shell heterostructures have been shown to reduce blinking, yet at a compromise with respect to enhanced multiphoton emission.⁷⁵

Due to reduced charge trapping on surface states, LHP NCs have become attractive as alternative single-photon emitters. Single particle spectroscopy at low temperatures has revealed that all CsPbX₃ NCs (X= Br/Cl, Br, I; cubes with the edge length of 8-14 nm in a polymer matrix) investigated thus far are capable of stable, fast and spectrally narrow single-photon emission (see Fig. 6).⁷³ The ensemble PL band of CsPbBr₂Cl NCs (Fig. 6a) shifts to lower energies upon cooling to 5 K (from 2.64 to 2.54 eV), concomitant with spectral narrowing (from 84 meV to 24 meV) due to reduced exciton-phonon coupling. This positive bandgap temperature coefficient, is directly opposite to that of conventional semiconductors (II-VI, III-V, and other systems), is characteristic also of other Pb-based semiconductors and originates from the strong Pb 6s contribution to the valence band (lifting the antibonding states). Individual CsPbBr₂Cl NCs exhibit much narrower PL linewidths of *ca.* 1 meV. In these cases, blinking-free PL with strongly reduced spectral diffusion (Fig. 6b) can last up to several hours. NCs of other compositions, such as CsPbBr₃ and CsPbI₃, exhibit equally narrow PL bands (as exemplified in Fig. 6c) with minimal to non-existent blinking, as reported by several groups.⁷⁷⁻⁷⁹

The most remarkable property of this emission, as reported recently,⁷⁴ is its high rate: radiative lifetimes as short as just a few hundreds of a picosecond, with pronounced

composition dependence, have been measured at cryogenic temperatures (Figure 6d). This behavior is remarkably different than that of CdSe-based NCs, which emit at up to a factor of 1000 slower (on the scale of microseconds) at cryogenic temperatures. The origin of the vastly different PL properties of CsPbX₃ NCs was explained by analyzing excitonic energy level ordering at the band-edge using DFT and k·p effective-mass calculations (Figure 6e)⁷⁴. It is notable that this work accounts for the orthorhombicity of the crystal structure, spin-orbit coupling and the existence of the Rashba effect.⁷⁸ In CdSe, as in nearly all molecular and semiconductor emitters, the lowest exciton state is optically “dark”, causing slow emission at low temperatures.⁸⁰ On the contrary, the triplet state in CsPbX₃ NCs is bright with high oscillator strength. The latter strongly accelerates the radiative recombination decay, rendering CsPbX₃ NCs among the fastest single-photon emitters reported to date.⁸¹ In addition, this triplet is three-fold orthogonally split, which agrees well with the experimental observation of three, linearly polarized, mutually orthogonal emission bands (Figure 6 e). Due to the small energy difference of just a few meV between the singlet and triplet states, these states are essentially mixed at RT. The low-temperature excitonic fine structure of CsPbBr₃ NCs was reported also elsewhere,⁷⁷ and it was suggested that the co-existence of several NC polymorphs, namely tetragonal and orthorhombic types, might explain that comparable numbers of NCs exhibit either 2 or 3 emission lines. Several groups have carried out low-temperature, single-dot spectroscopy in the presence of a magnetic field.^{77, 78} The nonlinear energy splitting between the polarized transitions versus magnetic field strength in these systems was observed recently.⁷⁸ At low magnetic field, the Rashba effect dominates the energetic splitting whereas the Zeeman effect becomes dominant at fields above 4 T. In that work the origin of the Rashba effect was attributed to a dynamic loss of the inversion symmetry in the orthorhombic CsPbBr₃, due to, for instance, Cs⁺ motion.

Several other important aspects concern the charged exciton (trion) dynamics in LHP NCs.⁷⁷ At relatively high excitation density, in addition to the multi-lined excitonic fine structure emission, a red-shifted single peak emerges, which has been assigned to trion recombination. Typical trion binding energies range from a few to up to 25 meV. Interestingly, the integrated PL intensities of the exciton and trion scale linearly with excitation power density, meaning that the quantum yield of this charged complex is not strongly affected by Auger recombination at low temperatures. This fact is in agreement with minimal single-dot blinking.⁷³

Obtaining well-behaved single-photon emission is by far more difficult in any systems at RT as compared to cryogenic temperatures. In order for NCs to act as an effective two-level system emitting single photons, efficient mechanisms to suppress multi-photon emission (such as the Auger process) are necessary. A simple spectral filtering would not be a practical solution to this problem since at room temperature, PL lines undergo homogenous broadening.⁸² Single-photon emission at RT, with strong photon anti-bunching, has been collected from single CsPbBr₃ and CsPb(Br/I)₃ NCs.⁸² The suppression of multi-photon events was attributed to fast non-radiative Auger recombination, which renders multi-exciton states virtually non-emissive (the fraction of multi photon coincidence events was ~6% on average). However, irreversible photo-degradation and blinking still occurred in these samples. On the contrary, other groups reported strongly reduced blinking, still with the retention of photon anti-bunching.⁸³ As with conventional QDs, the reported variability in the degree of blinking and stability can be attributed to the structural integrity of NCs, their surface chemistry and environmental effects. For instance, as discussed earlier, CsPbI₃ is known for its propensity to convert into a non-luminescent 1D-polymorph. The speed of this phase-transition is governed by its exposure to moisture and oxygen (although not by oxidation), thus explaining vastly different reports on the behavior of CsPbI₃ at a single-particle level. Furthermore, systematic studies of Auger recombination rates as a function of NC size and composition have only just begun.⁸⁴

With the fast development of RT-operational, single-photon emitters from LHPs, practical applications in quantum technologies might soon be within a reach. In the development of new devices, colloidal LHP NCs offer unique and advantageous attributes: low-cost synthesis, excellent spectral versatility (wavelength range, emission linewidth) and facile, solution-based deposition onto virtually any substrate. A specific future device, among others, is a single-photon LED (Fig. 6f), wherein LHP NCs will be integrated into a shot-noise limited, lightweight single photon source operating at RT and covering the entire visible spectrum, a technology outlook that is difficult to foresee with other existing quantum materials. Two possible device architectures are foreseen: (i) electrical injection of the carriers into a single perovskite NC as already being demonstrated in other quantum systems (organic molecules or NV-centers in diamond)^{85, 86} or (ii) integration of single NCs onto solid-state light sources (LEDs or lasers) as down-converting, single-photon sources. Ultrafast radiative recombination from individual LHP NCs will be beneficial, for instance,

for quantum key distribution, wherein high transmission bit rate is paramount. Furthermore, by combining NCs with different emission wavelengths on the same platform, an interesting opportunity might arise from wavelength-multiplexing, which is adapting old approaches from classical telecommunications to future, much-faster quantum communication. Ultra-fast LHP single photon sources might also find applications in advanced quantum metrology, from the calibration of photodetectors to the redefinition of the candela.

Open questions and beyond oD

Given the rate at which scientific results related to LHP NCs are published, it is not surprising that the literature is sometimes controversial; only through careful and less precipitous investigations can these ongoing issues be settled. For instance, CsPbBr₃ NCs were initially assigned as a cubic phase,⁹ but deeper analysis revealed that this phase is actually orthorhombic and exhibits highly dynamic structural disorder.⁸⁷ Even more debated issues are related to the correct assignment of optical and electronic structures to specific phases and compositions of cesium lead halides. Cesium, lead and bromine, for example, can crystallize into CsPbBr₃ perovskite or into non-perovskite phases, CsPb₂Br₅ and Cs₄PbBr₆. The latter non-perovskite has been reported to be green-luminescent by several groups, but at the similar wavelengths at which the emission of CsPbBr₃ is usually observed (ca. 520 nm).⁸⁸ Contrarily, other groups report larger bandgaps for both Cs₄PbBr₆ and CsPb₂Br₅, with no luminescence at all.^{46, 89} The compositional and structural complexity of LHP NCs is only starting to be fully recognized and rationalized.

It is clear that LHPs have enticed materials scientists, chemists and physicists to further development the, yet fundamental, research of LHP NCs, as well as finding ways to implement their applications. In our opinion, efficient pure-color or white-light generation with LHPs will gain increasing scientific interest and, very likely, will turn into a great commercial opportunity in the near future (in displays, lighting and other applications). In this regard, we would like to emphasize that colloidal APbX₃-type NCs are not the only promising forms of LHPs as versatile photonic sources. Quantum-confined LHPs can also be obtained in a stable bulk form. A notable case is that of the 2D Ruddlesden-Popper phases, in which 3D-like layers of [PbX₆] octahedra are electronically disconnected by the partial replacement of Cs/MA/FA cations with larger cations such as butylammonium. These can be

obtained as polycrystalline materials or as thin-films.^{90, 91} Such “2D” perovskites share many similarities with the aforementioned colloiddally synthesized LHP nanoplates/nanosheets, due to their strong quantum-confinement in one dimension. Combining the essential properties of colloidal LHP NCs and bulk 2D perovskites to achieve “multidimensional 3D/2D” LHP NCs has proved to be an interesting avenue of research, wherein the dimensionality of the electronic structure is engineered on both the atomic scale and nanoscale.⁹²⁻⁹⁴ This, and other research opportunities described in this review, will likely reveal their real potential soon.

BOX 1: History of CsPbX₃ and other LHP NCs

Although metal halide NCs may appear to be newcomers in materials science, this is rather a misconception. The earliest reports of particulate semiconductor systems known to exhibit crystal size effects on the excitonic optical absorption and emission spectra were CuCl nanocrystallites in a NaCl matrix (in 1950s)⁹⁵ and, a decade later, AgI colloids (1967).⁹⁶ Decades later, glass- and NaCl-embedded copper halide QDs played a historic role in the theoretical rationalization of quantum-size effects.^{97, 98}

The history of bulk cesium LHP materials extends much further back in time. The existence of crystalline compounds with composition CsPbX₃, as well as CsPb₂X₅ and Cs₄PbX₆, was first reported in the 1890s.⁹⁹ In 1957-1958, CsPbX₃ were found to crystallize in a perovskite-type lattice and exhibit photoconductivity.^{100, 101} High ionic conductivity, presently known as a reason for the electronic instability of perovskite materials as photovoltaics (PV) and a significant factor enabling fast ion-exchange in LHP NCs, was already reported for CsPbX₃ in the 1980s.¹⁰²

The line of research that would prove to be influential in the eventual discovery of colloidal CsPbX₃ NCs in 2015, began in the 1970s and concerned crystalline CsX materials doped with Pb²⁺ ions (typically at 0.01-1 at% doping levels). The interest in these materials stemmed from their potential as fast X-ray scintillators for the detection of ionizing radiation due to bright PL with short (ns- to sub-ns, or even tens of ps in chlorides) radiative lifetimes and high photon yield under high energy excitation. The RT-emission peak at ca. 2.45 eV (506 nm) of Pb-doped CsBr single crystals was discovered, at latest, in the 1970s¹⁰³, and its origin was attributed, until the mid-1990s, to the intra-atomic emission of Pb²⁺-related centers under the effect of Jahn-Teller splitting of the ns² cations. The more recent interpretation of the bright

PL in the visible spectrum of Pb-doped CsX melt-grown single crystals and thermally evaporated thin-film materials arose in the mid-1990s. The existence of few-nm sized, fluorescent inclusions of CsPbX₃ is now proposed to account for this bright PL, and the fact that the observed emission is often shifted to higher energies than that of bulk CsPbX₃ is attributed to quantum-size effects. For example, the PL of Pb²⁺ doped CsCl single crystals at 400-420 nm was interpreted to be due to excitonic emission from CsPbCl₃ clusters in 1995, and then also in Pb-doped CsBr.¹⁰⁴⁻¹⁰⁶ It is not surprising that CsPbX₃ nanoscale inclusions remained undetected for so long, owing to the combined effect of very low Pb-content, significant broadening of XRD reflections at sub-10 nm sizes and low electronic contrast between the CsX matrix and CsPbX₃ inclusions (*i.e.*, similar X-ray scattering factors). To induce the formation of nanosized CsPbX₃ inclusions in the CsX matrix on purpose and reproducibly, Pb-doped CsX single crystals grown by Bridgman or Stockbarger methods or as polycrystalline materials must be annealed for 10-100 hours at 150-300 °C to nucleate CsPbX₃. These annealing temperatures are sufficiently high to induce the motion and aggregation of ions, yet still below the melting points of the CsX matrix. Interestingly, the different PL spectra observed for samples annealed at 210 and 240 °C suggest the possibility that non-spherical, platelet-like CsPbCl₃ NCs were formed.¹⁰⁵ Multiple PL bands at shorter wavelengths (down to 390 nm) were quantitatively modelled as lattice-matched, atomically flat quantum wells of various thicknesses, with the thinnest being around 2.4 nm (corresponding to *ca.* 4 unit cells).

From the late 1990s on, considerable attention has also been devoted to thin CsPbX₃ films with reduced CsX excess, typically thermally evaporated and up to several μm in thickness.¹⁰⁷⁻¹⁰⁹ Very bright PL with quantum-size effects on excitonic emission was reported for CsPbBr₃ films that had initially been deposited in an amorphous phase at 77 K and which were then heated to RT to induce crystallization into a nanocrystalline state. Such films even exhibited stimulated emission at room-temperature under ns-pulsed excitation (0.5 ns, at 0.5 kW cm⁻² average threshold).¹⁰⁸

These early observations, as well as the widespread general attention for MAPbX₃ compounds as absorber materials for highly efficient PV in recent years and the notion that all-inorganic compositions of LHPs are generally superior for chemical stability, motivated the development of the hot-injection synthesis routes to CsPbX₃ NCs.⁹ These NCs were the

first in the colloidal NC family to exhibit bright PL over the entire visible spectral range, without electronic surface passivation; they are characterized by high PLQYs (up to >90%) and a narrow full width at half maximum (FWHM) of <100 meV (12-42 nm).

In a similar way, the history of organic-inorganic hybrid LHPs can be traced back to later 1970s, when the synthesis and crystal structures of MAPbX₃ were introduced.¹¹⁰ The structure and properties of FAPbBr₃ and FAPbI₃ have been reported only in the last decade. Works on particulate toluene dispersions of MA-based and other alkylammonium lead halides can be found since 2012-2013.^{111, 112} Much improved colloidal dispersibility of MAPbBr₃ nanoparticles was obtained with ligand-assisted re-precipitation method in the presence of long-chain ligands, first introduced by in 2014.⁸ Colloidal platelet-like and cuboidal FAPbBr₃ and FAPbI₃ NCs were reported since 2015.^{34, 113-115}

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a

Defect formation energy

b

Electronic structure

c Structure dynamics

Zwitterionic ligands:

Protective shell:

Matrix encapsulation:
halide salts (CsX , KX),
polymers, phosphate
and borosilicate glasses

Table 1. Comparison of the chemistry, durability and optical performance of LHP NCs with conventional NCs. Only NCs emissive in the visible spectral range are included.

	<p>Metal chalcogenide (II-VI) and pnictide (InP) core-only nanocrystals</p>	<p>Metal chalcogenide and pnictide core/shell nanocrystals</p>	<p>Lead halide perovskite nanocrystals</p>
Crystal structure	wurtzite, zinc-blende	wurtzite, zinc-blende	perovskite
Composition	CdSe, ZnSe, InP	CdSe/CdS, CdSe/CdZnS, InP/ZnS	(Cs,FA)PbX ₃ (X=Cl, Br, I), homogeneous, multinary compositions possible
Used in	no commercial use	LCD TV (Samsung, Sony, <i>etc.</i>), discontinued for Cd-based.	under development for LCD TV
Spectral range and efficiency	entire visible (400-700 nm) for II-VI and limited for InP (520-700 nm)	limited (510 - 650 nm)	entire visible (400-700 nm)
PL QY	low (0-10%)	high (up to 95%)	high (up to 99+%)
FWHM	narrow for II-VI (<25 nm; e.g. <100 meV), but limited for InP-based (ca. 40 nm at 530 nm PL peak)		narrow over entire visible range (<100 meV)
Defectiveness	low in binary compounds; high in multinary compositions (vacancies, antisites and interstitials)		intrinsically high (vacancies)
Synthesis	high-purity precursors and rigorous air-free synthesis; high-temperature	elaborate, lengthy synthesis; high-temperatures	facile synthesis; possible under ambient conditions
Post-synthesis tunability	only cation exchange		cation exchange (both A and B sites) and anion exchange
Surface ligands	highly versatile organic and inorganic surface functionalization		limited affinity to the surfaces; new ligand chemistries are urgently needed
Heteronanostructures	yes (complex core shells/dumbbells/Janus <i>etc.</i>)		none to date
Thermal stability	stable	stable	limited to below 100 °C due to low

			melting points
Oxidative and photostability	low to moderate	high	high
Solvent compatibility	compatible with all solvents, including water		finite solubility in water and many polar solvents, insoluble in all others
RoHS compliance	limited for CdSe-based (100 ppm limit for Cd), unlimited for InP-based		limited but higher than for CdSe-based (1000 ppm limit for Pb)
Single-dot PL			
Single-photon emission	yes	yes	yes
Multi-exciton emisison	low yield	high yield	high yield
Blinking	yes	reduced	reduced
Photobleaching	fast	moderate	moderate
Emission rate	~10 ns (RT), sub-μs (5K)	10-100 ns (RT), sub-μs (5K)	1-50 ns, longer for iodides (RT), sub-ns (5K)