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# **1** Genesis, Challenges and Opportunities for Colloidal Lead Halide

# 2 Perovskite Nanocrystals

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4 Quinten A. Akkerman<sup>1,2</sup>, Gabriele Rainò,<sup>3,4</sup> Maksym V. Kovalenko<sup>3,4\*</sup> and Liberato Manna<sup>1,5\*</sup>

- <sup>1</sup>Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
- 6 <sup>2</sup>Università degli Studi di Genova, Via Dodecaneso, 31, 16146, Genova, Italy
- 7 <sup>3</sup>Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir
- 8 Prelog Weg 1, CH-8093 Zürich, Switzerland
- 9 <sup>4</sup>Laboratory for Thin Films and Photovoltaics, Empa Swiss Federal Laboratories for Materials Science and
- 10 Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
- <sup>5</sup>Kavli Institute of Nanoscience and Department of Chemical Engineering, Delft University of Technology, PO
- 12 Box 5, 2600AA, Delft, The Netherlands
- 14 \*e-mail: mvkovalenko@ethz.ch; liberato.manna@iit.it
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Abstract. Lead halide perovskites (LHPs) in the form of nanometer-sized colloidal crystals 17 (nanocrystals, NCs) have attracted the attention of diverse materials scientists due to their 18 19 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 20 are highly tolerant to structural defects and surface states. Therefore, they cannot be 21 approached with the same experimental mindset and theoretical framework as conventional 22 semiconductor NCs. In this review, we discuss LHP NCs historical and current research 23 pursuits, challenges in applications, and the related present and future mitigation strategies 24 explored. 25

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One way of introducing lead halide perovskites nanocrystals (LHP NCs) is to place them in 27 the context of research on colloidal semiconductors NCs, which started several decades ago 28 and that is still flourishing. A historical account on LHP NCs research, beginning from early 29 studies on metal halides, is reported in Box 1. The next section will give a snapshot of the 30 main structural features of LHP NCs and their synthesis approaches. The challenges related 31 to the stability of LHP NCs and possible strategies to address this issue will be discussed in 32 the subsequent sections. Finally, prospects for applications in consumer optoelectronics, as 33 well as in single-photon sources will be provided. For other aspects of colloidal LHP NCs, we 34 refer the reader to several recent reviews.<sup>1-3</sup> 35

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#### 37 Soft ionic crystal structure and facile synthesis of LHP NCs

Traditional colloidal semiconductor NCs, which have been actively investigated since the 38 discovery of the hot-injection, high-temperature synthesis of Cd chalcogenide NCs,<sup>4</sup> 39 primarily constitute binary compounds with rather simple crystal structure types: 40 tetrahedrally-bonded compounds of zinc-blende (chalcogenides: ZnS, ZnSe, CdS, CdSe, 41 HgTe; pnictides: InP, InAs) or wurtzite (ZnS, ZnSe, CdS, CdSe) structure, or face-centered 42 rock-salt-type compounds (PbS, PbSe). In this review, those semiconductor NCs which are 43 spheres or cubes smaller than 20 nm and are therefore quantum-confined in all three 44 dimensions, are also termed quantum dots (QDs). The anions and cations in the crystals of 45 46 these traditional semiconductor NCs have crystallographically identical positions/sublattices. LHPs (Fig. 1a) instead crystallize in the cubic APbX<sub>3</sub>-type perovskite 47 lattice [where A is methylammonium (MA,  $CH_3NH_3^+$ ), formamidinium (FA,  $CH(NH_2)_2^+$ ) or 48 cesium (Cs<sup>+</sup>), X is one or more halides (Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>)] or its octahedrally tilted variants, 49 50 isostructural to traditional oxide perovskites such as CaTiO<sub>3</sub>. These structures are characterized by the 3-dimensional (3D) interconnection of their [PbX<sub>6</sub>]<sup>4-</sup> octahedra, with 51 the A-site cation residing in the large voids in between. The typically cubic or orthorhombic 52 symmetries of these lattices are apparent in the commonplace observation of the cuboidal 53 54 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<sub>6</sub> 55 framework due to their geometric fitness within a twelve-coordinate A-site. Larger or 56 smaller cations favor the formation of polymorphs of a lower dimensionality (oD, 1D or 2D), 57

with edge- or face-sharing of the octahedra, and as a consequence, larger and often indirect energy bandgaps.<sup>5</sup> 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.<sup>6</sup> Here we emphasize that unlike the oxide perovskites, LHPs exhibit much lower melting points (400-500 °C in CsPbX<sub>3</sub>) due to lower ionic charges and larger interatomic distances, as well as a higher propensity to thermal decomposition (below 300 °C for MA- andFA-based materials).

64 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 65 for the synthesis, surface functionalization and processing of LHP NCs. Conventional QDs 66 67 require elevated synthesis temperatures in order to promote crystallization. Existing hotinjection synthesis methods, typically at temperatures of 100-350 °C, are ideal for NCs of 68 69 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 70 the standard solution phase fashion, even at temperatures as high as 400 °C.<sup>7</sup> Their synthesis 71 72 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 73 seconds even at room-temperature (RT), from a vast selection of precursors.<sup>8-10</sup> Initially, the 74 synthesis and processing of CsPbX<sub>3</sub> NCs were primarily approached with the same methods 75 76 as conventional QDs. For example, ligand-assisted hot-injection synthesis (RT-200 °C) was used to synthesize the first CsPbX<sub>3</sub> NCs.<sup>9</sup> An alternative strategy is the ligandassisted re-77 precipitation method, wherein an ionic solution of the respective ions (A<sup>+</sup>, Pb<sup>2+</sup> and X<sup>-</sup>) in a 78 polar solvent is rapidly destabilized by mixing with a non-solvent inducing a burst of 79 nucleation, as originally proposed for MAPbBr<sub>3</sub> NCs.<sup>8</sup> Both methods are applicable to the 80 whole APbX<sub>3</sub> family and the reaction conditions can be adjusted to yield non-cuboidal 81 shapes, such as nanoplatelets, nanosheets and nanowires.<sup>2, 11-13</sup> Other facile routes to 82 colloidal LHPs include microwave-assisted synthesis, sonication of the precursors in a 83 solvent/ligand mixture and ball-milling.<sup>14-16</sup> Automated, high-throughput screening, such as 84 using robotics<sup>17</sup> or microfluidics equipped with on-line optical characterization,<sup>18</sup> can also 85 86 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 89 convert to cuboidal or other irregular shapes, or recrystallize into the bulk material upon 90 isolation and purification, upon concentration or dilution, or under strong UV irradiation. 91 In the case of nanowires, satisfactory durability is found only in wires with a diameter of 10-92 200 nm. Thus far, the synthesis of stable, few-nm sized QDs or atomically-sized clusters has 93 remained elusive for LHPs. Sub-5 nm quantum-confined LHP NCs could be produced, but 94 only via non-colloidal approaches, by the ligand-free, templated growth of LHP in ordered 95 mesoporous silica scaffolds.<sup>19, 20</sup> 96



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**Figure 1. Colloidal lead halide perovskite nanocrystals.** (a) The APbX<sub>3</sub> perovskite 99 structure with 3D-corner-sharing octahedra. Two typical structures are shown: cubic 100 (MAPbX<sub>3</sub>, FAPbX<sub>3</sub>; two unit cells shown) on the left and orthorhombic (CsPbX<sub>3</sub>) on the 101 right; (b) high-angle annular dark-field scanning transmission electron micrograph 102 (HAADF-STEM) of a single, cube-shaped CsPbBr<sub>3</sub> NC, with 15 nm edge length; (c) 103 104 photograph of highly luminescent colloidal LHP NCs (from left to right, CsPbBr<sub>3</sub> with emission peak at 520nm,  $CsPb(Cl/Br)_3$  emitting at 450 nm and  $FAPb(Br/I)_3$  emitting at 105 640nm). Figure (c) is courtesy of Dr. Yevhen Shynkarenko. 106

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#### 108 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 116 LHPs are highly tolerant to the material's defects and surfaces.<sup>21</sup> This defect tolerance seems 117 to be a fortunate coincidence of several factors. Firstly, out of a large variety of conceivable 118 point defects, only vacancies (primarily A- and X-site vacancies, Fig. 2a) are characterized by 119 sufficiently low formation energies and are therefore exclusively observed. Interstitial and 120 anti-site defects, which would form deep trap states in the electronic structure, are almost 121 absent<sup>22, 23</sup> since ions in the perovskite lattice are energetically difficult to misplace. Secondly, 122 the shallow character of the vacancy-related states is due to unique specifics of the bonding 123 in LHPs, namely the antibonding character of the valence band maxima (with mixed I 5p and 124 Pb 6s character; Fig. 2b) and spin-orbit effects in the conduction band (which has a 125 predominant Pb 6p character). NC surfaces can simply be imagined as a plane of vacancies 126 and should therefore exhibit similarly benign behavior as vacancies. This intuition explains 127 the observation of high PL QYs without surface passivation in LHP NCs. However, it should 128 be also pointed that LHP NCs are not entirely defect-free, as PL QYs are normally reported in 129 the range of 80-95% in the green-red region and down to 10-20% at the blue border region 130 (close to 400 nm, i.e., CsPbCl<sub>3</sub>). Yet, these values greatly exceed any other non-passivated QD 131 material in the same range of wavelengths. There exist multiple reports of the beneficial 132 effects of various post-synthetic ligand treatments, such as with thiocyanates, PbBr<sub>2</sub> or 133 trioctylphosphine-PbI<sub>2</sub>, raising the PL QY close to 100%,<sup>24, 25</sup> presumably due to the improved 134 passivation of under-coordinated Pb ions. Thirdly, the soft and dynamic nature of the 135 perovskite lattice is such that this material has been defined a "crystalline liquid", to highlight 136 the simultaneous emergence of its crystalline and liquid-like properties. These features seem 137 to protect its carriers from trapping and scattering.<sup>26</sup> Together with its partial ionic character, 138 the intense structural dynamics of PbX lattices at RT leads to the coupling of electrons and 139 140 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 141 carrier scattering, both mutually and with charged defects and optical phonons.<sup>26, 27</sup> In hybrid 142 perovskites, the A-site molecular rotational motion on the (sub-) ps timescale also allows for 143 the screening of hot carriers,<sup>26, 27</sup> which potentially creates the possibility of harnessing the 144 hot-carrier energy in order to improve the efficiency of solar cells or to observe hot-carrier PL. 145

146 The defect tolerance of LHPs, emerging from the s and p contributions of the Pb atoms, is 147 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,<sup>28</sup> 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 155 defect-tolerance in perovskite NCs emerges from three distinctive features: their crystal 156 structure, favoring the formation of vacancies but no other point defects; their peculiar 157 electronic structure that makes vacancies benign; and their dynamic lattice effects such as 158 formation of polarons, thereby preventing carriers from trapping. (a) Typical point defects in 159 LHPs, including vacancies, interstitial and anti-site atoms, in order of increasing formation 160 energy (or decreasing probability of occurrence), and their depths in the bandgap. (b) 161 Schematic representation of electronic band structure of typical defect-intolerant 162 In conventional semiconductors, such as cadmium semiconductors and LHPs. 163 chalcogenides, the bandgap is formed between bonding ( $\sigma$ ) and antibonding ( $\sigma$ \*) orbitals. 164 Point defects or dangling bonds emerge as weak bonding or non-bonding states within the 165 bandgap. In LHPs, the bandgap is formed between two anti-bonding orbitals. Defects states 166 will thus form only shallow traps or will be enclosed in the conduction or valance band, and 167 will thus not strongly influence the radiative recombination and other optical properties. (c) 168 Schematic representation of local structural deformation of the Pb-Br framework that, 169 combined with a charge carrier (electron or hole), forms a polaron. 170

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#### 172 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,<sup>29</sup> or on 178 carboxylate or phosphonate (X-type) ligands attached at surface metal adatoms.<sup>29, 30</sup> LHP 179 NCs are terminated by oleylammonium bromide and/or oleylammonium carboxylate.<sup>30</sup> Each 180 of these coordinates to the surface as an ionic pair: ammonium groups displace a surface A-181 182 site cation, whereas carboxylates (bromides) act as surface anions. These ligands tend to auickly desorb (Fig. 3a).<sup>30</sup> The most dramatic consequence of such loose ligand binding is 183 the difficulty met in isolating and purifying colloids using standard methods for QDs, 184 namely by a repetitive precipitation with a non-solvent followed by redispersion in a pure 185 solvent. More static surface coordination might be expected from the ligands containing 186 several anchoring groups, such as zwitterionic molecules (Fig. 3b), containing quaternary 187 ammonium and carboxylate groups (or sulfonate, phosphonate, or other groups). 188 Oligomeric ligands with a larger number of these charged groups and long hydrocarbon 189 chains per molecule can be envisaged as well. 190

191 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 192 NCs upon exposure to such solvents. This problem will remain difficult to mitigate until a 193 strategy for the full encapsulation of individual LHP NCs in an inert shell is identified (for 194 instance, within silica, titania, alumina, salts with extremely low solubility products such as 195  $BaSO_4$  or similar, see Fig. 3c). A classical approach to coating LHP NCs with  $SiO_{27}$  however, 196 would require adapting a sol-gel process such as the Stöber method. This has not been 197 demonstrated yet, presumably due to the necessity of using alcohols or similar protic polar 198 solvents. As a result of LHP NCs being so fragile, complex morphologies, such as core-shell 199 200 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 201 202 far lesser but still significant extent, FAPbX<sub>3</sub>. MA-based LHP compounds have a low energy 203 of formation and even decompose at RT. This decomposition is reportedly accelerated by 204 heat, light, moisture and oxygen, as well as by the high surface area of the NCs, yielding PbX<sub>2</sub> and several volatile products (CH<sub>3</sub>NH<sub>2</sub>, HI, I<sub>2</sub> and other species). Thus, future 205 applications are foreseen to be primarily limited to FA- and Cs-based LHP NCs. Poor 206 207 thermal stability is another major challenge for nearly all future applications of LHP NCs. 208 Hybrid organic-inorganic LHPs decompose before melting (MAPbI<sub>3</sub> at *ca.* 150-200 °C; FAPbI<sub>3</sub> at *ca.* 290-300 °C), while the melting points of fully inorganic LHPs are slightly higher (450-500 °C for CsPbBr<sub>3</sub> and CsPbI<sub>3</sub>). LHP NCs are all highly prone to sintering. This poses a great challenge for any device architecture relying on the retention of quantumconfined states in a densely packed array of LHP NCs or for devices operating at elevated temperatures, such as lasers or remote phosphors.

214 Another form of structural lability is observed in red-emitting CsPbI<sub>3</sub> (both in the bulk and in NCs). In this case, the Cs<sup>+</sup> ions are too small to be included in a 3D perovskite Pb-iodide 215 cage, causing the transition to another polymorph of a lower dimensionality and, hence, a 216 217 much wider bandgap.<sup>31, 32</sup> It has, on the other hand, also often been reported that a variation 218 in the purification procedure and the exclusion of air during handling and storage do extend the lifetime of metastable 3D-CsPbI<sub>3</sub> phases.<sup>33-35</sup> Considerable work has been done, both with 219 NCs and thin films, to stabilize CsPbI<sub>3</sub> by partially replacing Cs<sup>+</sup> with larger cations (the 220 foremost example being FA<sup>+</sup>), and by partially replacing I<sup>-</sup> with Br<sup>-</sup>.<sup>34, 36</sup> A similar stabilization 221 effect was reported for the replacement of Pb<sup>2+</sup> with smaller cations such as Mn<sup>2+</sup> and Bi<sup>3+</sup>, as 222 shown by a retention of bright red PL.<sup>37-39</sup> 223

Beyond solution-phase chemistry, another underestimated opportunity might deserve 224 further attention, especially in the context of the thermal and environmental stabilization of 225 LHPs. Dynamic structural disorder on fs-ps timescales suggests that it might be very 226 difficult if not impossible to coat LHP NCs with crystalline shells with interfaces that are 227 structurally stable. A promising alternative path to stable LHP emitters is the melt-growth of 228 glass-embedded LHP NCs (Figure 3d), such as in recent reports employing typical phosphate 229 or borosilicate glasses.<sup>40-43</sup> Thus-obtained crystalline NCs, whose size is tunable by melt-230 quenching and by adjusting the subsequent thermal conditions, are surrounded by an 231 amorphous, chemically stable, water- and oxygen-impermeable glass matrix. Such glass-232 embedded NCs, easily obtainable in powdered form by a grinding step after quenching the 233 melt, can be easily integrated into any down-conversion-based application of LHP emitters -234 235 be it backlighting in displays or as a remote phosphor in lighting.

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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.

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## 246 From labile LHP NCs to nanocrystal transformers

The high ionicity and structural instability of LHP NCs can also be exploited for post-247 synthetic transformations, either with the retention of the original crystal structure, or 248 through reorganization into a new crystal structure. In well-controlled cases, such 249 transformations take place while preserving the overall NC size and shape, or at least the 250 initial size uniformity, as depicted in Figure 4.<sup>34, 44-47</sup> Perhaps the most striking example is 251 that of anion exchange,<sup>44, 45</sup> whose fast rate can be attributed to the high concentration of 252 halide vacancies and the high mobility of singly charged halide anions. The PL color of LHP 253 NCs can be adjusted by anion-exchange to any wavelength in the visible spectrum, starting 254 from just one progenitor NC sample (Fig. 4a). It has further been established that mixed-255 256 halide compositions in NCs are more easily retained than in thin-films, which suffer from photo-induced halide-ion segregation.<sup>48</sup> In metal chalcogenide NCs, only the cations have 257 been manipulated in a similarly facile way.<sup>49</sup> In LHPs, the high plasticity of the lattice 258 enables the exchange of both cations and anions. The A-site cations can be partially or fully 259 exchanged ( $Cs^+$  with FA<sup>+</sup> or MA<sup>+</sup>, and in reverse),<sup>34</sup> whereas Pb<sup>2+</sup> can be partially exchanged 260 with Sn<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> cations (Fig. 4b,c).<sup>47</sup> Similarly, doping CsPbCl<sub>3</sub> NCs with several at% 261

of  $Mn^{2+}$  yields strongly orange-luminescent NCs (PL QY = 58%; emission from the 262 dopant).<sup>50, 51</sup> Extensive restructuring of LHP NCs is also possible, by either eliminating or 263 adding ions (Fig. 4d-g). For instance, upon removing <sup>3</sup>/<sub>4</sub> of the Pb atoms in the form of PbX<sub>2</sub>, 264 CsPbX<sub>3</sub> NCs can transform into Cs<sub>4</sub>PbX<sub>6</sub> NCs,<sup>52</sup> which are characterized by a structure in 265 which all  $[PbX_6]^{4-}$  octahedra are disconnected from each other (oD-perovskite). Back 266 conversion into CsPbX<sub>3</sub> NCs can be accomplished by re-inserting PbX<sub>2</sub> into Cs<sub>4</sub>PbX<sub>6</sub> NCs or 267 by extracting CsX by the action of suitable ligands.<sup>46, 53, 54</sup> It is also possible to extract PbBr<sub>2</sub> 268 from CsPbBr<sub>3</sub> NCs, forming CsBr NCs or, vice versa, to convert pre-synthesized CsBr NCs 269 into  $CsPbX_3$  NCs. These conversions are readily observable owing to a color change due to 270 the large difference in bandgap energies (2.43 eV for CsPbBr<sub>3</sub>, 3.95 eV for Cs<sub>4</sub>PbBr<sub>6</sub> and 7.3 271 eV for CsBr). Such chemical transformations, using a presently unexplored variety of A- and 272 273 B-site metals, will enable the discovery of new functional metal halide NCs, including those 274 that cannot be obtained by direct synthesis.



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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<sup>+</sup> with, for instance, FA<sup>+</sup>, which is key to the stability of iodides. (d) Phase-transformation from CsPbX<sub>3</sub> to Cs<sub>4</sub>PbX<sub>6</sub> and CsX via reactions with Pb<sup>2+</sup> or PbX<sub>2</sub>. (e-g) TEM images of NCs obtained by deliberate transformations between different Cs-Pb-Br compounds.

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LHP NCs vs. conventional QDs. A comparison between the physical and electronic properties of 286 conventional QDs and LHP NCs is shown in Table 1. For decades, the primary challenge 287 facing semiconductor NCs was the suppression of the role of mid-gap surface traps that 288 render practically all as-synthesized semiconductor NCs that emit in the visible range poorly 289 290 luminescent. This has been conventionally mitigated by the elaborate synthesis of sophisticated, core-shell CdSe-CdZnS NCs, via decoupling of the excitonic recombination 291 from surface states. These NCs feature high PL QYs of up to 95-100%, narrow emission lines 292 and excellent long-term stability, and they are currently applied as down-converting 293 294 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 295 QYs even when the synthesis was performed under ambient conditions and/or without pre-296 purified chemicals. Small FWHM and high PL QYs are also repeatedly reported with more 297 complex, mixed-cation Cs/FA and mixed halide (Cl/Br, Br/I) stoichiometries.<sup>34</sup> Solution-298 based compositional engineering has shown to be possible on all three lattice sites within 299 LHPs, such as in FA<sub>0.75</sub>Cs<sub>0.25</sub>Sn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>3</sub> or (Cs/Rb/FA/MA)Pb(Br/I)<sub>3</sub>.<sup>55, 56</sup> However, it is 300 difficult to achieve a combination of high optoelectronic quality and atomistic homogeneity 301 in multinary metal chalcogenide NCs (CuInS<sub>2</sub>, CuIn<sub>x</sub>Ga<sub>(1-x</sub>)Se<sub>2</sub> and Cu<sub>2</sub>ZnSnS<sub>4</sub>)<sup>57</sup> and it 302 remains completely elusive for pnictide NCs. Typically, for the tetrahedrally-bonded 303 compounds, site disorder (interstitial and anti-site atoms) and phase inhomogeneities are 304 enhanced in NCs as compared to the bulk. In contrast, the LHP lattice, wherein ions cannot 305 easily be misplaced due to their specific sizes, coordination numbers and ionic charges, is 306 307 intrinsically immune to such defects. With regards to multinary LHP NCs such as (Cs/FA)Pb(Br/I)<sub>3</sub>, a detailed structural analysis is still pending and will be crucial for further 308 taming the presently unstable red and near-IR emitting LHP NCs. 309

# 310 Table 1. Comparison of the chemistry, durability and optical performance of LHP

311 NCs with conventional NCs. Only NCs emissive in the visible spectral range are included.

|                               | Metal chalcogenide (II-VI)<br>and pnictide (InP) core-<br>only nanocrystals     | Metal chalcogenide and<br>pnictide core/shell<br>nanocrystals | Lead halide perovskite<br>nanocrystals   |  |
|-------------------------------|---|---|--|--|
| Crystal structure             | wurtzite, zinc-blende   | wurtzite, zinc-blende   | perovskite   |  |
| Composition                   | CdSe, ZnSe, InP   | CdSe/CdS, CdSe/CdZnS, InP/ZnS                                 | (Cs,FA)PbX3(X=Cl, Br, I),homogeneous,multinarycompositions possible                |  |
| Used in                       | no commercial use   | LCD TV (Samsung, Sony, etc.), discontinued for Cd-based.      | under development for LCD TV   |  |
| Spectral range and efficiency | entire visible (400-700 nm) for II-<br>VI and limited for InP (520-700<br>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<br>40 nm at 530 nm PL peak)                 | meV), but limited for InP-based (ca.                          | narrow over entire visible range<br>(<100 meV)                                     |  |
| Defectiveness                 | low in binary compounds; high in antisites and interstitials)                   | multinary compositions (vacancies,                            | intrinsically high (vacancies)   |  |
| Synthesis                     | high-purity precursors and<br>rigorous air-free synthesis; high-<br>temperature | elaborate, lengthy synthesis; high-<br>temperatures           | facile synthesis; possible under<br>ambient conditions                             |  |
| Post-synthesis<br>tunability  | ability 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;<br>new ligand chemistries are<br>urgently needed |  |
| Heteronanostructu<br>res      | yes (complex core shells/dumbbells/Janus etc.)                                  |   | 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<br>compatibility      | compatible with all solvents, including water                                   |   | finite solubility in water and many<br>polar solvents, insoluble in all<br>others  |  |
| RoHS compliance               | ce limited for CdSe-based (100 ppm limit for Cd), unlimited for InP-based       |   | limited but higher than for CdSe-<br>based (1000 ppm limit for Pb)                 |  |
| Single-dot PL                 |   |   |  |  |
| Single-photon<br>emission     | yes   | yes   | yes  |  |
| Multi-exciton                 | low yield   | high yield  | high yield   |  |

| emisison       |                             |                                |  |
|----------------|-----------------------------|--------------------------------|--|
| Blinking       | yes                         | reduced                        | reduced  |
| Photobleaching | fast                        | moderate                       | moderate   |
| Emission rate  | ~10 ns (RT),<br>sub-µs (5K) | 10-100 ns (RT),<br>sub-µs (5K) | 1-50 ns, longer for iodides (RT),<br>sub-ns (5K) |

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#### 313 Consumer optoelectronic devices with LHP NCs

The wide color gamut of the PL of LHP NCs meets the existing color standards for display 314 applications (Figure 5a). The small FWHM of this PL of ≤100 meV corresponds to just 18-20 315 316 nm in the green region around 520-530 nm (CsPbBr<sub>3</sub>, FAPbBr<sub>3</sub> NCs), making such emitters valid contenders with traditional green phosphors. A promising near-future application for 317 LHP NCs is therefore in LCD backlighting, for which color-pure green and red emitters with 318 PL peaks centered at 530 nm and 630 nm are desired. Closely related prospective 319 320 applications include remote phosphors for lighting and color-controlling and colorenhancing films in portable gadgets. The InP-based NCs currently used in Samsung SUHD 321 TV displays have broader PL bands (FWHM  $\approx$  40 nm at 530 nm), which are difficult to 322 improve upon due to inherent compositional and morphological inhomogeneities in the 323 few-nm-sized InP-based emissive cores. Towards display applications, the incorporation of 324 325 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 326 327 stability of such emitters were indeed obtained by incorporating LHP NCs in waternonpermeable polymers and into salt matrixes (potassium halides or Cs<sub>4</sub>PbX<sub>6</sub>).<sup>58-60</sup> 328

329 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 330 diodes (LEDs). Thus far, LEDs based on CsPbBr<sub>3</sub> NCs are the most studied, with typical 331 external quantum efficiencies (EQEs) of  $6.3\%^{6_1}$  and  $8.7\%^{6_2}$ . The former study reported a peak 332 luminance of over 15'000 cd/m<sup>2</sup>, while the latter reported a more modest value of 1'660 cd/m<sup>2</sup>. 333 Both studies highlight the importance of purifying LHP NCs from excess ligands. Red CsPbI<sub>3</sub> 334 NC LEDs showed an EQE of 7.3% and a peak luminance of 435 cd/m<sup>2</sup> at 688 nm.<sup>63</sup> It remains 335 difficult to construct efficient blue LEDs with perovskite NCs, where the best example is that 336 of MAPbBr<sub>1.5</sub>Cl<sub>1.5</sub> NCs,<sup>64</sup> which exhibit an EQE of 1.18% and a peak luminance of 2473 cd/m<sup>2</sup> at 337

338 445 nm. For the blue-most CsPbCl<sub>3</sub> NCs, the highest achieved EQE to date is only 0.61% and 339 the corresponding luminance was 11 cd/m<sup>2</sup> (at 404 nm).<sup>63</sup>

LHP NCs also show great promise as versatile solution-based precursors for the low-340 temperature fabrication of absorber layers for PV (Figurer 5b).<sup>65</sup> Solar cells with efficiencies 341 up to 10.8% were demonstrated using CsPbI<sub>2</sub> NC thin-films deposited by multiple rounds of 342 sequential spin-coating and ligand-removal steps.<sup>33</sup> We expect further progress in this 343 direction, utilizing more complex compositions of LHP NCs. This is motivated by recent 344 trends in thin-film LHP PV where power conversion efficiencies exceeding 20% have been 345 reported, by employing mixed-cation and mixed-anion compositions such as 346 (Cs/Rb/FA/MA)Pb(Br/I)<sub>3</sub>.<sup>56</sup> NC-based synthesis routes to such complex thin-films might have 347 certain inherent advantages. For example, although the deposition of such films requires the 348 solubilisation of all of the precursor salts in polar solvents, coating, annealing and 349 recrystallization of the LHPs in a single step, the use of LHP NCs separates the mixing of ions, 350 film-formation and crystallization into three different steps. The nonpolar solvents used for 351 depositing NCs might also be advantageous, for example, in maintaining solvent 352 orthogonality in the deposition from solution of consecutive layers of the device. LHP NCs 353 are also unique in their ability to form bulk heterojunctions with other solution-processable 354 355 materials such conductive polymers, fullerenes or other QDs.



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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).

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## 362 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 363 upon introduction into consumer electronics. One should note here that the industrialized 364 world has been exposed to massive amounts of lead over the decades. A now infamous, 365 volatile compound, tetraethyl lead, has been used since the 1920s as an additive to fuels, and 366 367 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, 368 Pb remains widely used in, for example, lead-acid batteries, solder in silicon solar cells, 369 piezoelectrics and even as a white pigment  $(PbO_2)$ . 370

371 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 372 lead is 1000 ppm by weight in any continuous solid component of the device, which is not as 373 stringent as the current limit for cadmium (100 ppm by weight). Current Cd-based QD TV 374 displays require only about 1.5 mg of Cd (for a 55 inch display).<sup>66</sup> For LHPs, one could 375 376 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 377 PL efficiencies at the same PL wavelengths (530 and 630 nm). This corresponds to sub-1000 378 ppm concentrations of Pb within the 50-100 µm thick polymer film, hence not requiring an 379 RoHS exemption. With regard to consumer electronics, the recycling policies for Pb are well 380 detailed and are highly efficient. 381

Efforts are underway to find environmentally benign and, at the same time, chemically 382 robust alternatives to lead-based chemistries for optoelectronic applications. As discussed 383 above, defect-tolerant semiconductors are those in which both the s and p electrons of a 384 metal hybridize to form the valence and conduction bands. In accordance with this 385 principle, Sn<sup>2+</sup> and Ge<sup>2+</sup> analogues of LHPs do exhibit bright emissions but, unfortunately, 386 are highly unstable. Even trace oxygen quantities cause degenerative p-type doping in tin 387 and germanium perovskites through oxidation. Furthermore, Sn-based analogues of LHPs 388 are, from a toxicity point of view, not ideal alternatives.<sup>67</sup> High stability and bright emission 389 have been reported for oD-perovskite-like structures  $(C_4N_2H_{14}Br)_4SnX_6 (X = Br, I)$ ,<sup>68</sup> but with 390 a very large FWHM of above 100 nm at RT. 391

The solar cell community has contributed great effort in the search for lead-free, LHP-like semiconductors.<sup>69</sup> In particular, the replacement of  $Pb^{2+}$  with oxidatively stable Bi<sup>3+</sup> is an attractive option. However, such ternary halides are structurally very different from LHPs since they typically crystallize into oD or 2D networks of M-X polyhedra, usually with indirect band gaps, such as in  $Cs_3M_2X_9$  (M = Sb, Bi, In).<sup>70</sup> So far, these phases have not exhibited efficient PL at RT. To retain the 3D-interconnection of octahedra, double perovskite compositions of  $A_2M^{1+}M^{3+}X_6$  have been investigated, such as  $Cs_2AgBiCl_6$  and  $Cs_2AgInCl_6.^{71, 72}$  Such compounds have not yet shown photophysical characteristics on par with LHPs, and they exhibit indirect band gaps, making them unsuitable as emitters.

401 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 402 analogues, the chances of developing bright, LHP-like nanoscale emitters are, in our 403 opinion, far greater. The reasons for this optimism are as follows. First, while PV materials 404 must have bandgaps beyond 700 nm, LHP NCs as bright emitters are primarily needed to 405 function with bandgaps of 450-700 nm. Hence, many materials discarded by the PV research 406 community might be perfectly suited for constructing NC emitters. Second, the spatial 407 confinement of carriers in NCs usually drastically enhances the PL QY. To this end, and in 408 retrospect, the bright green PL from CsPbBr<sub>3</sub> could have been discovered much earlier; this 409 compound has been known for over 100 years, and all that was needed to be done was 410 intense mechanical grinding of the bulk material. However, this idea would have been hard 411 to conceive of since bulk CsPbBr<sub>3</sub> is essentially non-luminescent. In conclusion, it seems to 412 413 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 414 415 they become luminescent.





417 Figure 6. LHP NCs as single-photon sources. (a) Typical ensemble absorption and PL spectra from CsPbBr<sub>2</sub>Cl NCs recorded at RT, an ensemble PL spectrum recorded at T = 5 K 418 and three representative single-dot spectra. (b) Time series of PL from a single CsPbBr<sub>2</sub>Cl 419 420 NC at 6 K, showing stable emission without blinking and with minimal spectral diffusion. (c) Representative single-dot spectra from CsPbX<sub>3</sub> NCs of various compositions. (d) Time-421 resolved PL traces for NCs of various compositions. (e) Polarization dependent single 422 423 CsPbBr<sub>2</sub>Cl 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 424 (top-left) of the band-edge excitonic states in CsPbX<sub>3</sub> NCs comprising a three-fold split 425 bright triplet state and a dark singlet state. (f) Future LEDs featuring individually 426 addressable single NC emitters. Figures (a & b) are adapted with permission from Ref.73 427

428 Figure (c), courtesy of IBM Research – Zurich (M. A. Becker, T. Stöferle, R. F. Mahrt). Figures

429 (d & e) are adapted with modifications from Ref.<sup>74</sup>

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#### 431 LHP NCs as single-photon sources

432 In addition to conventional optoelectronic devices, colloidal semiconductor NCs can be employed as non-classical light sources (single photon emitters)<sup>75</sup> that might play a pivotal 433 role in future quantum technologies (such as quantum cryptography, quantum sensing and 434 quantum communication).<sup>76</sup> At this time, most such studies have concerned CdSe-based 435 NCs. The common challenges of such applications, including emission intermittency 436 (blinking), photo-instability and spectral diffusion, originate from factors that are inherent 437 438 to the QD material (for instance, surface traps, enhanced Auger processes, facile photoionization, photo-oxidation and other environmental effects).<sup>75</sup> Specially designed 439 core-shell heterostructures have been shown to reduce blinking, yet at a compromise with 440 respect to enhanced multiphoton emission.75 441

Due to reduced charge trapping on surface states, LHP NCs have become attractive as 442 alternative single-photon emitters. Single particle spectroscopy at low temperatures has 443 revealed that all CsPbX<sub>3</sub> NCs (X= Br/Cl, Br, I; cubes with the edge length of 8-14 nm in a 444 polymer matrix) investigated thus far are capable of stable, fast and spectrally narrow single-445 photon emission (see Fig. 6).73 The ensemble PL band of CsPbBr<sub>2</sub>Cl NCs (Fig. 6a) shifts to 446 lower energies upon cooling to 5 K (from 2.64 to 2.54 eV), concomitant with spectral 447 narrowing (from 84 meV to 24 meV) due to reduced exciton-phonon coupling. This positive 448 bandgap temperature coefficient, is directly opposite to that of conventional 449 semiconductors (II-VI, III-V, and other systems), is characteristic also of other Pb-based 450 semiconductors and originates from the strong Pb 6s contribution to the valence band 451 (lifting the antibonding states). Individual CsPbBr<sub>2</sub>Cl NCs exhibit much narrower PL 452 linewidths of ca. 1 meV. In these cases, blinking-free PL with strongly reduced spectral 453 diffusion (Fig. 6b) can last up to several hours. NCs of other compositions, such as CsPbBr<sub>3</sub> 454 and CsPbI<sub>3</sub>, exhibit equally narrow PL bands (as exemplified in Fig. 6c) with minimal to non-455 existent blinking, as reported by several groups.77-79 456

The most remarkable property of this emission, as reported recently,<sup>74</sup> 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 459 460 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 461 vastly different PL properties of CsPbX<sub>3</sub> NCs was explained by analyzing excitonic energy 462 level ordering at the band-edge using DFT and  $k \cdot p$  effective-mass calculations (Figure 6e)<sup>74</sup>. 463 It is notable that this work accounts for the orthorhombicity of the crystal structure, spin-464 orbit coupling and the existence of the Rashba effect.<sup>78</sup> In CdSe, as in nearly all molecular 465 and semiconductor emitters, the lowest exciton state is optically "dark", causing slow 466 emission at low temperatures.<sup>80</sup> On the contrary, the triplet state in CsPbX<sub>3</sub> NCs is bright 467 with high oscillator strength. The latter strongly accelerates the radiative recombination 468 decay, rendering CsPbX<sub>3</sub> NCs among the fastest single-photon emitters reported to date.<sup>81</sup> In 469 addition, this triplet is three-fold orthogonally split, which agrees well with the experimental 470 observation of three, linearly polarized, mutually orthogonal emission bands (Figure 6 e). 471 Due to the small energy difference of just a few meV between the singlet and triplet states, 472 these states are essentially mixed at RT. The low-temperature excitonic fine structure of 473 CsPbBr<sub>3</sub> NCs was reported also elsewhere,<sup>77</sup> and it was suggested that the co-existence of 474 several NC polymorphs, namely tetragonal and orthorhombic types, might explain that 475 comparable numbers of NCs exhibit either 2 or 3 emission lines. Several groups have carried 476 out low-temperature, single-dot spectroscopy in the presence of a magnetic field.<sup>77, 78</sup> The 477 nonlinear energy splitting between the polarized transitions versus magnetic field strength 478 in these systems was observed recently.<sup>78</sup> At low magnetic field, the Rashba effect dominates 479 the energetic splitting whereas the Zeeman effect becomes dominant at fields above 4 T. In 480 that work the origin of the Rashba effect was attributed to a dynamic loss of the inversion 481 symmetry in the orthorhombic CsPbBr<sub>3</sub>, due to, for instance, Cs<sup>+</sup> motion. 482

Several other important aspects concern the charged exciton (trion) dynamics in LHP 483 NCs.<sup>77</sup> At relatively high excitation density, in addition to the multi-lined excitonic fine 484 485 structure emission, a red-shifted single peak emerges, which has been assigned to trion 486 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 487 excitation power density, meaning that the quantum yield of this charged complex is not 488 489 strongly affected by Auger recombination at low temperatures. This fact is in agreement with minimal single-dot blinking.73 490

Obtaining well-behaved single-photon emission is by far more difficult in any systems at 491 492 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 493 (such as the Auger process) are necessary. A simple spectral filtering would not be a 494 practical solution to this problem since at room temperature, PL lines undergo homogenous 495 broadening.<sup>82</sup> Single-photon emission at RT, with strong photon anti-bunching, has been 496 collected from single CsPbBr<sub>3</sub> and CsPb(Br/I)<sub>3</sub> NCs.<sup>82</sup> The suppression of multi-photon 497 events was attributed to fast non-radiative Auger recombination, which renders multi-498 exciton states virtually non-emissive (the fraction of multi photon coincidence events was 499 ~6% on average). However, irreversible photo-degradation and blinking still occurred in 500 these samples. On the contrary, other groups reported strongly reduced blinking, still with 501 the retention of photon anti-bunching.<sup>83</sup> As with conventional QDs, the reported variability 502 in the degree of blinking and stability can be attributed to the structural integrity of NCs, 503 their surface chemistry and environmental effects. For instance, as discussed earlier, CsPbI<sub>3</sub> 504 is known for its propensity to convert into a non-luminescent 1D-polymorph. The speed of 505 this phase-transition is governed by its exposure to moisture and oxygen (although not by 506 oxidation), thus explaining vastly different reports on the behavior of CsPbl<sub>3</sub> at a single-507 particle level. Furthermore, systematic studies of Auger recombination rates as a function of 508 NC size and composition have only just begun.<sup>84</sup> 509

With the fast development of RT-operational, single-photon emitters from LHPs, practical 510 applications in quantum technologies might soon be within a reach. In the development of 511 new devices, colloidal LHP NCs offer unique and advantageous attributes: low-cost 512 synthesis, excellent spectral versatility (wavelength range, emission linewidth) and facile, 513 514 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-515 516 noise limited, lightweight single photon source operating at RT and covering the entire 517 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 518 the carriers into a single perovskite NC as already being demonstrated in other quantum 519 systems (organic molecules or NV-centers in diamond)<sup>85, 86</sup> or (ii) integration of single NCs 520 521 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, 522

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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.

#### 530 Open questions and beyond oD

Given the rate at which scientific results related to LHP NCs are published, it is not 531 surprising that the literature is sometimes controversial; only through careful and less 532 precipitous investigations can these ongoing issues be settled. For instance, CsPbBr<sub>3</sub> NCs 533 were initially assigned as a cubic phase,<sup>9</sup> but deeper analysis revealed that this phase is 534 actually orthorhombic and exhibits highly dynamic structural disorder.<sup>87</sup> Even more debated 535 issues are related to the correct assignment of optical and electronic structures to specific 536 phases and compositions of cesium lead halides. Cesium, lead and bromine, for example, 537 can crystallize into CsPbBr<sub>3</sub> perovskite or into non-perovskite phases, CsPb<sub>2</sub>Br<sub>5</sub> and 538 Cs<sub>4</sub>PbBr<sub>6</sub>. The latter non-perovskite has been reported to be green-luminescent by several 539 groups, but at the similar wavelengths at which the emission of CsPbBr<sub>3</sub> is usually observed 540 (ca. 520 nm).<sup>88</sup> Contrarily, other groups report larger bandgaps for both Cs<sub>4</sub>PbBr<sub>6</sub> and 541 CsPb<sub>2</sub>Br<sub>5</sub>, with no luminesce at all.<sup>46, 89</sup> The compositional and structural complexity of LHP 542 NCs is only starting to be fully recognized and rationalized. 543

544 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 the 545 implement their applications. In our opinion, efficient pure-color or white-light generation 546 with LHPs will gain increasing scientific interest and, very likely, will turn into a great 547 548 commercial opportunity in the near future (in displays, lighting and other applications). In 549 this regard, we would like to emphasize that colloidal APbX<sub>3</sub>-type NCs are not the only 550 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, 551 552 in which 3D-like layers of [PbX<sub>6</sub>] octahedra are electronically disconnected by the partial replacement of Cs/MA/FA cations with larger cations such as butylammonium. These can be 553

obtained as polycrystalline materials or as thin-films.<sup>90, 91</sup> Such "2D" perovskites share many 554 similarities with the aforementioned colloidally synthesized LHP nanoplates/nanosheets, 555 due to their strong quantum-confinement in one dimension. Combining the essential 556 properties of colloidal LHP NCs and bulk 2D perovskites to achieve "multidimensional 557 3D/2D" LHP NCs has proved to be an interesting avenue of research, wherein the 558 dimensionality of the electronic structure is engineered on both the atomic scale and 559 nanoscale.<sup>92-94</sup> This, and other research opportunities described in this review, will likely 560 reveal their real potential soon. 561

### 562 BOX 1: History of CsPbX<sub>3</sub> 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)<sup>95</sup> and, a decade later, AgI colloids (1967).<sup>96</sup> Decades later, glass- and NaCl-embedded copper halide QDs played a historic role in the theoretical rationalization of quantum-size effects.<sup>97, 98</sup>

The history of bulk cesium LHP materials extends much further back in time. The existence of crystalline compounds with composition CsPbX<sub>3</sub>, as well as  $CsPb_2X_5$  and  $Cs_4PbX_6$ , was first reported in the 1890s.<sup>99</sup> In 1957-1958, CsPbX<sub>3</sub> were found to crystallize in a perovskite-type lattice and exhibit photoconductivity.<sup>100, 101</sup> 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 CsPbX<sub>3</sub> in the 1980s.<sup>102</sup>

The line of research that would prove to be influential in the eventual discovery of colloidal 576 CsPbX<sub>3</sub> NCs in 2015, began in the 1970s and concerned crystalline CsX materials doped with 577 Pb<sup>2+</sup> ions (typically at 0.01-1 at% doping levels). The interest in these materials stemmed from 578 their potential as fast X-ray scintillators for the detection of ionizing radiation due to bright 579 580 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 581 Pb-doped CsBr single crystals was discovered, at latest, in the 1970s<sup>103</sup>, and its origin was 582 attributed, until the mid-1990s, to the intra-atomic emission of Pb<sup>2+</sup>-related centers under the 583 effect of Jahn-Teller splitting of the ns<sup>2</sup> cations. The more recent interpretation of the bright 584

PL in the visible spectrum of Pb-doped CsX melt-grown single crystals and thermally 585 586 evaporated thin-film materials arose in the mid-1990s. The existence of few-nm sized, fluorescent inclusions of CsPbX<sub>3</sub> is now proposed to account for this bright PL, and the fact 587 that the observed emission is often shifted to higher energies than that of bulk CsPbX<sub>3</sub> is 588 attributed to quantum-size effects. For example, the PL of Pb<sup>2+</sup> doped CsCl single crystals at 589 400-420 nm was interpreted to be due to excitonic emission from CsPbCl<sub>2</sub> clusters in 1995, an 590 then also in Pb-doped CsBr<sup>104-106</sup> It is not surprising that CsPbX<sub>3</sub> nanoscale inclusions 591 remained undetected for so long, owing to the combined effect of very low Pb-content, 592 significant broadening of XRD reflections at sub-10 nm sizes and low electronic contrast 593 between the CsX matrix and CsPbX<sub>3</sub> inclusions (*i.e.*, similar X-ray scattering factors). To 594 595 induce the formation of nanosized CsPbX<sub>3</sub> inclusions in the CsX matrix on purpose and reproducibly, Pb-doped CsX single crystals grown by Bridgman or Stockbarger methods or as 596 597 polycrystalline materials must be annealed for 10-100 hours at 150-300 °C to nucleate CsPbX<sub>3</sub>. These annealing temperatures are sufficiently high to induce the motion and aggregation of 598 599 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-600 spherical, platelet-like CsPbCl<sub>3</sub> NCs were formed.<sup>105</sup> Multiple PL bands at shorter wavelengths 601 (down to 390 nm) were quantitatively modelled as lattice-matched, atomically flat quantum 602 wells of various thicknesses, with the thinnest being around 2.4 nm (corresponding to ca. 4 603 unit cells). 604

From the late 1990s on, considerable attention has also been devoted to thin CsPbX<sub>3</sub> films with reduced CsX excess, typically thermally evaporated and up to several  $\mu$ m in thickness.<sup>107-</sup> <sup>109</sup> Very bright PL with quantum-size effects on excitonic emission was reported for CsPbBr<sub>3</sub> 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<sup>-2</sup> average threshold).<sup>108</sup>

These early observations, as well as the widespread general attention for MAPbX<sub>3</sub> 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 CsPbX<sub>3</sub> NCs.<sup>9</sup> These NCs were the 616 first in the colloidal NC family to exhibit bright PL over the entire visible spectral range, 617 without electronic surface passivation; they are characterized by high PLQYs (up to >90%) 618 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 619 1970s, when the synthesis and crystal structures of MAPbX<sub>3</sub> were introduced.<sup>110</sup> The structure 620 and properties of FAPbBr<sub>3</sub> and FAPbI<sub>3</sub> have been reported only in the last decade. Works on 621 particulate toluene dispersions of MA-based and other alkylammonium lead halides can be 622 found since 2012-2013.<sup>111, 112</sup> Much improved colloidal dispersibility of MAPbBr<sub>3</sub> nanoparticles 623 was obtained with ligand-assisted re-precipitation method in the presence of long-chain 624 ligands, first introduced by in 2014.<sup>8</sup> Colloidal platelet-like and cuboidal FAPbBr<sub>3</sub> and FAPbI<sub>3</sub> 625 NCs were reported since 2015.<sup>34, 113-115</sup> 626

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Cubic and orthorombic APbX<sub>3</sub>





APbX<sub>3</sub> collodial dispersions











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

|                                  | Metal chalcogenide (II-VI)<br>and pnictide (InP) core-<br>only nanocrystals                                  | Metal chalcogenide and<br>pnictide core/shell<br>nanocrystals                      | Lead halide perovskite nanocrystals   |
|----------------------------------|--|--|---|
| Crystal structure                | wurtzite, zinc-blende  | wurtzite, zinc-blende  | perovskite  |
| Composition                      | CdSe, ZnSe, InP  | CdSe/CdS, CdSe/CdZnS, InP/ZnS  | (Cs,FA)PbX <sub>3</sub> (X=Cl, Br, l),<br>homogeneous, multinary<br>compositions possible |
| Used in                          | no commercial use  | LCD TV (Samsung, Sony, etc.),<br>discontinued for Cd-based.                        | under development for LCD TV  |
| Spectral range and<br>efficiency | entire visible (400-700 nm) for II-<br>VI and limited for InP (520-700<br>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><br>40 nm at 530 nm PL peak) |  | narrow over entire visible range<br>(<100 meV)  |
| Defectiveness                    | low in binary compounds; high in multinary compositions (vacancies, antisites and interstitials)             |  | intrinsically high (vacancies)  |
| Synthesis                        | high-purity precursors and<br>rigorous air-free synthesis; high-<br>temperature                              | elaborate, lengthy synthesis; high-<br>temperatures                                | facile synthesis; possible under<br>ambient conditions                                    |
| Post-synthesis<br>tunability     | only cation exchange   |  | cation exchange (both A and B sites) and anion exchange                                   |
| Surface ligands                  | highly versatile organic and inorgan   | limited affinity to the surfaces;<br>new ligand chemistries are<br>urgently needed |   |
| Heteronanostructu<br>res         | yes (complex core shells/dumbbells/Janus etc.)   |  | 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<br>compatibility     | compatible with all solvents, including water                          |                                | finite solubility in water and many<br>polar solvents, insoluble in all<br>others |  |
| RoHS compliance              | limited for CdSe-based (100 ppm limit for Cd), unlimited for InP-based |                                | limited but higher than for CdSe-<br>based (1000 ppm limit for Pb)                |  |
| Single-dot PL                |  |                                |   |  |
| Single-photon<br>emission    | yes  | yes                            | yes   |  |
| Multi-exciton<br>emisison    | low yield  | high yield                     | high yield  |  |
| Blinking                     | yes  | reduced                        | reduced   |  |
| Photobleaching               | fast   | moderate                       | moderate  |  |
| Emission rate                | ~10 ns (RT),<br>sub-µs (5K)  | 10-100 ns (RT),<br>sub-µs (5K) | 1-50 ns, longer for iodides (RT),<br>sub-ns (5K)                                  |  |