# Optically Pumped White Light-Emitting Diodes Based on Metal Halide Perovskites and Perovskite-Related Materials

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## Abstract

**Optically pumped white light emitting diodes (WLEDs), consisting of blue/ultraviolet (UV) LED chips and down conversion phosphors, have a wide range of applications in our daily life, such as full color display and solid-state lighting. While remarkable progresses in light quality, device efficiency, and lifetime have been achieved during the last two decades, many challenges remain in optically pumped WLEDs, and searching for low cost high performance down conversion phosphors is still of great interest. Recently, metal halide perovskites have emerged as a highly promising new generation of light emitters for their exceptional optical properties with high quantum efficiencies and color tunability, which have also inspired researchers to investigate their derivatives. In this perspective, we briefly review the progresses during the last few years in the development of metal halide perovskites and perovskite-related materials as down conversion phosphors for optically pumped WLEDs. We also highlight some major issues and challenges that need to be addressed to enable perovskite-based light emitters to possibly replace currently used rare-earth doped inorganic phosphors and quantum dots.**

## I. Introduction

In 2014, the Nobel Prize for physics was awarded to a trio of scientists in Japan and the US for the invention of efficient blue light-emitting diodes (LEDs), which together with down conversion phosphors have enabled bright and energy-saving solid-state white light sources. During the last two decades, these LED-based light sources have revolutionized the display and lighting industries, for their numerous advantages (e.g. energy efficient, long lifetime, eco-friendly, color tunable) over conventional technologies, such as incandescent and fluorescent lighting.[1, 2] The performance of representative optically pumped WLEDs are summarized in table 1. The three major device characteristics are color rendering index (CRI), correlated color temperature (CCT), and luminous efficiency. While optically pumped WLEDs have steadily become the mainstream, there is still plenty of room for further improvement before they can really be considered as perfect light sources. One of the opportunities lies on the development of new generation light emitters that could overcome the drawbacks of existing commercially available phosphors, i.e. rare-earth doped inorganic phosphors[3-18] and quantum dots.[19-29] Inorganic phosphors based on rare earth elements are not sustainable and their preparation requires energy consuming high temperature processes.[19, 20] Moreover, the low-color purity of inorganic phosphors leads to poor white light quality. Quantum dots possess improved color purity, but mass production of luminescent and stable monodisperse quantum dots is very sophisticated and costly. Therefore, searching for low cost, color tunable, and eco-friendly light emitters is still of great interest.

**Table 1**: Device characteristics of common optically pumped WLEDs

| Phosphor | CRI | CCT | Luminous Efficiency (lm/W) | Ref |
|---|---|---|---|---|
| **YAG:Ce** | 80 | 3000 | 160 | Commercial WLED |
| **YAG:Ce, $K_2SiF_6:Mn^{4+}$** | 89.9 | 3900 | 116 | [30] |
| **YAG:Ce, CdSe/ZnSe** | 92.3 | - | 77.1 | [31] |

Recently, metal halide perovskites and their low-dimensional derivatives have emerged as highly promising light emitters that could serve as down conversion phosphors for optically pumped WLEDs. Electrically driven green,[32] red[33] and NIR[34, 35] metal halide perovskite light-emitting diodes with efficiencies near the theoretical limit have also been demonstrated. The remarkable photoluminescence properties of $ABX_3$ (A = Cs, $CH_3NH_3$ or $NH_2CHNH_2$, B = Pb or Sn, and X = Cl, Br, I, or their mixtures) perovskites, in particular their nanocrystals (NCs), include narrow emission covering the whole of the visible region with small full width at half maximum (FWHM) of less than 20 nm, high photoluminescence quantum efficiencies (PLQEs) of up to near-unity, and exceptional color tunability via structural and compositional controls. Since the first report of using this class of hybrid materials as down conversion phosphors for WLEDs in 2015,[36] tremendous efforts in developing highly luminescent and stable perovskite NCs, as well as novel encapsulation techniques, have led to remarkable improvements of device efficiency and stability.[37] For their low-dimensional derivatives, in which metal halides form 2D, 1D, or 0D structures at the molecular level, highly efficient broadband emissions with PLQEs of up to near-unity could be realized.[38] Of particular interest are corrugated-2D and 1D organic metal halide hybrids that exhibit intrinsic white light emissions, making them highly promising single component white phosphors for optically pumped WLEDs.

In this perspective, we provide a brief review on the development of optically pumped WLEDs based on metal halide perovskite NCs and low-dimensional organic metal halide hybrids. Notable achievements during the last few years will be presented, followed by discussions on the issues and challenges for these materials. The outlook will be provided in the end, with proposed research to eventually make metal halide perovskites and perovskite-based materials commercially viable phosphors for optically pumped WLEDs.

## II. Metal halide perovskite NCs for optically pumped WLEDs

Metal halide perovskite NCs, such as $CsPbX_3$, have attracted great research attention with potential applications in various types of optoelectronic devices,[39-41] owing to their exceptional optical properties, i.e. highly tunable narrow emissions over the entire visible region with PLQEs of up to near-unity.[37, 42-46] Since the first report of perovskite NCs synthesis by Perez-Prieto and colleagues in 2014,[47] a variety of approaches have been developed to prepare metal halide perovskite NCs, including hot-injection,[37] ligand-assisted reprecipitation (LARP),[48] microwave irradiation,[49] *in-situ* formation,[50-52] and template-assisted methods (Figure 1a-b).[53-56] Typical electron transmission micrographs of colloidal NCs synthesized using the hot injection method are shown in Figure 1c-d. For photoluminescence color tuning, two major strategies have been developed to achieve bandgap control of perovskite NCs, one relying on the manipulation of halide compositions,[37] and the other through quantum-size effects[57] (Figure 1e-f). The excellent photoluminescence properties of perovskite NCs make them highly promising down conversion phosphors for optically pumped WLEDs. After the first demonstration of WLEDs using perovskite NCs in 2015, with a luminous efficiency of 48 lm/W,[48] the device characteristics of WLEDs as well as their stabilities have improved steadily during the last few years, thanks to continuous efforts on material development and device optimization with several notable achievements summarized below.

In 2015, Kovalenko et. al. reported the colloidal synthesis of $CsPbX_3$ NCs with narrow emissions (FWHM 12 - 42 nm), high PLQEs (50 – 90%) and tunable emission color spanning the entire visible region (410-700 nm) through halide mixing and substitution.[37] Following that, perovskite NCs have been widely investigated as light emitters for various optoelectronic devices.[58-64] Optically pumped WLEDs (schematics shown in Figure 2a) have been a natural application for perovskite NCs, with the utilization of their exceptional photoluminescence properties. For instance, Dong and colleagues reported the preparation of brightly luminescent and color-tunable colloidal $CH_3NH_3PbX_3$ NCs with high PLQEs via a LARP strategy. Optically pumped WLEDs using green emitting $CH_3NH_3PbBr_3$ quantum dots and red emitting $K_2SiF_6:Mn^{4+}$ (KSF:Mn) phosphor as color converters showed an optimized luminous efficiency of 48 lm/W at a driving current of 4.9 mA.[48] Due to the limited thermal stability of organic-inorganic perovskite NCs, all-inorganic $CsPbX_3$ perovskites have been widely considered to be more suitable and promising for lighting applications. Meyns and coworkers have used poly(maleic anhydride-alt-1-octadecene) (PMA) coated $CsPbX_3$ NCs to demonstrate WLEDs with 4.5 lm/W luminous efficacy, a CRI of 72.4 and a CCT of 3665 K (Figure 2b).[65] Because of the narrow emissions of perovskite NCs with low spectral coverage, the white emission had less-than-optimal CRI. Moreover, the red emitting NCs based on iodide anions experienced photo-induced phase transition from highly emissive cubic phase to less emissive tetragonal and orthorhombic phases. This, in turn, led to spectral instability in the fabricated WLEDs and significant changes in CRI and CCT values. To address the limited spectral coverage and low CRI values, six-color multipackage WLEDs were demonstrated with a luminous efficiency of 62 lm/W, a CRI of 96, and CCT of 6500K (Figure 2c).[60] Wang and coworkers showed WLEDs based on pure all-inorganic red emitting perovskite NCs combined with YAG:Ce, exhibiting warm white light with a CCT of 3328 K and a CRI of 84.7.[62] Similarly, Liu et. al. used green perovskite NCs along with KSF:Mn to demonstrate WLEDs with color coordinates of (0.271,0.232).[61]

In the above discussed cases, non-perovskite phosphors have often been used together with perovskite NCs to achieve white emission. Alternatively, dual emission can be realized by doping other metals in perovskite NCs, such as $Mn^{2+}$, $Bi^{3+}$ and $Eu^{2+}$.[66-72] Chen et. al. exploited the exciton energy transfer from a $CsPb(Cl/Br)_3$ host to $Mn^{2+}$ dopant to synthesize blue LED excitable $SiO_2$ coated green and orange NCs, and subsequently fabricated WLEDs with tunable CCT (5942 K - 6636 K) and CRI (82.7 - 84.6) and a maximum luminous efficiency of 40 lm/W (Figure 2d).[73] Wang et. al. reported pure white emission with *Commission internationale de l'éclairage* (CIE) coordinates of (0.35, 0.32) from $Mn^{2+}$-doped mixed halide (Cl/Br) perovskite nanoplatelets.[67] Similarly, Cui and colleagues prepared $Mn^{2+}$ and $Eu^{3+}$ doped all-inorganic $CsPbCl_3$ NCs encapsulated into a $SiO_2$ film.[68] Upon encapsulation, the PLQE increased from 3.52% and 21.01% to 49.00% and 50.84% for $Eu^{3+}$ and $Mn^{2+}$ doped $CsPbCl_3$ NCs, respectively. Song et. al. reported $Bi^{3+}/Mn^{2+}$ co-doped $CsPbCl_3$ perovskite NCs that exhibited tunable emissions with CCT ranging from 19,000 K to 4250 K under UV excitation, by simply adjusting the dopant concentrations.[69]

Although great success has been achieved in incorporating perovskite NCs into WLEDs, there are still many issues and challenges, including thermal instability, particle aggregation, anion exchange, ligand dissociation, and so on. To address these issues, various surface treatments have been developed for perovskite NCs. Wang and colleagues introduced a small molecule 1-tetradecylphosphonic acid (TDPA) as a coating agent to improve the stability of $CsPbBr_3$ NCs. The resulting NCs not only retained a high PLQE, but also exhibited better moisture and thermal stability. The WLEDs, using green-emitting $CsPbBr_3$/TDPA NCs and red-emitting KSF:Mn phosphors as down converters, showed a high luminous efficiency of 63 lm/W.[74] In addition, the WLEDs showed high device stability, where 90% of the luminous efficiency was retained for 15 hours operating under a relative humidity (RH) of 60% (Figure 2e). Similarly, various polymers have been used for surface treatment to improve the stability of perovskite NCs. For instance, Chen et al. prepared $CsPbBr_3$ NCs/ ethylene vinyl acetate composite films.[75] Rogach's group reported water resistant perovskite NC powders via surface protection of $CsPbX_3$ with a polyhedral oligomeric silsesquioxane (POSS), which prevents anion exchange between perovskite NCs of different compositions mixed together in the solid state with preservation of their distinct emissions.[76] The resulting WLEDs based on mixtures of green emitting POSS-$CsPbBr_3$ and red-emitting POSS-$CsPb(Br/I)_3$ nanocrystal powders showed CIE coordinates of (0.349, 0.383), CRI value of 81 and luminous efficiency of 14.1 lm/W. The use of other polymeric coatings, such as poly(maleic anhydride-alt-1-octadecene) (PMA)[59] and poly(maleic anhydride-alt-1-octadecene)(PMAO)[77], has also been reported. Interestingly, by using perovskite NCs as photointiators for polymerization of high molecular weight polymers, Tan et al. reported highly efficient perovskite-polymer nanocomposites as down-conversion layers.[78] Silica coating has also been found to be an effective way to improve the stability of perovskite NCs against moisture ingress. Liu and coworkers synthesized silica-coated perovskite NCs, which showed increased stability under ambient conditions.[79] By using those nanocomposites as down converters, WLEDs with CIE coordinates of (0.31, 0.34) and CRI of 85 were fabricated. He and colleagues demonstrated stable $CsPbX_3$ nanocomposites by the in-situ anchoring of $CsPbX_3$ NCs onto octadecyl-/propylamine-capped silica particles ($SiO_2$ NPs). WLEDs fabricated using this strategy featured a CIE color coordinate (0.3225, 0.3468) and a luminous efficiency of 26.3 lm /W.[80] Moreover, Song et al. prepared highly stable and water-soluble $CsPbX_3/SiO_2$ nanocomposites by encapsulating the $CsPbX_3$ (X=Cl, Br, I) perovskite NCs into silica nanoplates. The WLEDs based on these nanocomposites exhibited color coordinates of (0.30, 0.31), luminous efficiency of 35.32 lm/W and improved resistance to moisture.[81] $SiO_2$ coating has also been shown to improve the moisture and photo stability of perovskite NCs. For instance, Li et al. showed $MAPbBr_3$ NCs embedded in $SiO_2$ were markedly more stable under light stress and high humidity compared to unencapsulated NCs (Figure 2f).[82] Other strategies employed to enhance the stability of perovskite NCs for efficient WLEDs include using an inorganic salt framework[83] and embedding NCs in polymer matrices.[84]

## III. Low-Dimensional Organic Metal Halide Hybrids: Broadband Emitters as Down-Conversion Phosphors

Materials that exhibit intrinsic white emissions are of great interest for optically pumped WLEDs. The use of such materials has the potential to overcome problems observed in the conventional optically pumped WLED based on phosphor mixtures, such as efficiency losses due to cross and self-absorption, and the change of the white light quality over time due to different ageings of mixed phosphors.[9, 85] Recently, low-dimensional metal halide hybrids have been demonstrated to show broadband white emission suitable for WLED applications. Low-dimensional metal halide hybrids are bulk assemblies of metal halide polyhedrons into sheets, wires, and molecular/cluster species isolated from each other by large organic cations at the molecular level.[86] Single crystalline low-dimensional metal halide hybrids can show the intrinsic properties of individual metal halide sheets, chains, or polyhedra, as a result of strong quantum confinement and site isolation.

## i. Two-dimensional (2D) Metal Halide Hybrids

### a. 2D (<100> Oriented) metal halide hybrids

In 2014, Karunadasa et. al. reported <100> oriented 2D sheets of $PbCl_4$ separated by 2,2′-(ethylenedioxy)bis(ethylammonium) (EDBE) organic cations.[87] This 2D organic metal halide hybrid displayed broadband white emission with CIE coordinate of (0.33, 0.39), a CCT of 5509 and a CRI of 81. The emission profile displayed a broad spectrum (FWHM = 208 nm) attributed to emission from self-trapped states and a small shoulder peak at higher energy coming from free exciton recombination. Although the white light quality was promising, this material suffered from a low PLQE (2 %). Similarly, a white light emitting 2D organic metal halide hybrid, composed of $[PbBr_4]^{2-}$ sheets and *cis*-1,3-bis(methylaminohydrobromide)cyclohexane ($CyBMA^{2+}$) cations, were reported by Mathews and colleagues.[88] The authors speculated the "softness" and flexibility of organic spacer cations lead to strong exciton-phonon interactions to yield self-trapped excitons. Radiative decays of self-trapped excitons as well as free excitons were believed to be responsible for the broad white emission at room temperature. The PLQE of this white emission was reported to be around 1.5%. Although phenethylammonium ($C_6H_5C_2H_4NH_3^+$) has been used to form $[PbBr_4]^{2-}$ and $[PbI_4]^{2-}$ inorganic sheets with narrow emissions, surprisingly, its combination with $[PbCl_4]^{2-}$ sheets has been shown to produce a broad white emission.[89] The broad emission was attributed to self-trapping caused by distortion in the organic spacers. Similarly, Luo et. al. demonstrated an ultra-high CRI (≈ 91) white emission and a higher PLQE of 3.37 % by using (1, 2mept = 2-methyl-1,5-diaminopentane) ($2mept^{2+}$) to create 2D metal halide sheets of $[PbBr_4]^{2-}$.[90] <100> oriented 2D organic metal halide hybrids were also obtained by varying the position of methoxy groups on methoxy benzylammonium at ortho, meta and para positions.[91] Large lattice distortion and exciton self-trapping was demonstrated by using the ortho isomer of methoxy benzylammonium to form $[PbBr_4]^{2-}$ 2D sheets, which led to broad white emission. Optically pumped WLEDs fabricated using this material as a phosphor showed a high color rendering index (CRI, Ra = 86) and a luminous efficiency of 16 lm/W.

### b. Corrugated 2D (<110> oriented) Metal Halide Hybrids

Recently, corrugated-2D lead halide perovskites have emerged as another highly promising class of single component white emitters. These materials are achieved by slicing the 3D cubic $ABX_3$ perovskite structure along the (110) crystallographic plane. In 2014 Karanudasa et al.[92] reported corrugated-2D lead halides (N-MEDA) $PbBr_4$ (N-MEDA =N-methylethane- 1,2-diammonium) that displayed a broad band emission with a maximum around 560 nm from self-trapped excitons and a shoulder at higher energy from free excitons upon UV-excitation. Substituting a small amount of Br with Cl in (N-MEDA)$PbBr_{4-x}Cl_x$ tuned the color of the emission to achieve "warm" and "cold" white light with PLQEs between 0.5 to 1.5 % and improved the CRI from 82 to 85. Later, the same group reported another corrugated-2D structure (EDBE)$PbBr_4$ (EDBE = 2,2′ (ethylenedioxy)bis(ethylammonium)) that also shows white light emission but with a higher PLQE of 9% and a CRI of 84 (Figure 3a-b).[87] Our group employed a facile one pot synthesis to prepare microcrystalline (EDBE)$PbBr_4$ that possesses a PLQE of 18%, much higher than that of bulk crystal counterparts. The microscale crystals that can be suspended in solutions also have much better film processability than bulk crystals. [93] A UV-pumped WLED based on these microcrystals was demonstrated, which showed cold white light with a CIE of (0.30, 0.42) at 3.0 V correlated to CCT of 6519 K and good stability with little to no voltage dependence of emission (Figure 3 d-e). Luo et al. synthesized N-(3-aminopropyl)imidazole tetrachloro-lead that exhibits warm white light with a CRI of 93, which is the highest CRI ever reported for a corrugated-2D perovskite.[94] Besides "2×2" corrugated structures, other corrugated-2D structures with white emissions have been developed. For instance, Kanatzidis and colleagues reported a "3×3" corrugated α-(DMEN)$PbBr_4$ (DMEN=2-(dimethylamino) ethylamine) that can be obtained from the kinetically stable β-(DMEN)$PbBr_4$ and display cold white emission with a CRI of 73.[95] Nonetheless, the PLQEs and stabilities of these materials are still too low to satisfy the requirements of down conversion phosphors (PLQE of > 90%) for UV-pumped WLEDs.

The intriguing optical properties of 2D and corrugated-2D metal halide hybrids have been investigated using structural, spectroscopic, and theoretical studies to reveal the origin of the broad white emission.[96-99] Because of the soft and deformable nature of the inorganic lattices, strong exciton-phonon interactions are present in these materials during photoexcitation.[96] This exciton-phonon coupling leads to the formation of self-trapped states and multiple color centers in the form of polaron-excitons localized in the inorganic lattice.[98] Radiative decay of the excited state via these self-trapped intra-bandgap emissive states leads to the observed large Stokes-shift and emission broadening.[100] The excited state dynamics of these systems is illustrated in the configurational coordinate diagram in Figure 3c. Moreover, the increase in photoluminescence intensity with excitation power without saturation indicates the transient nature of these self-trapped states. The presence of emissive intra-gap states was also confirmed through transient absorption spectroscopy which showed photo-induced absorption band covering the whole of the visible spectrum.[98] In-depth treatment of the excited state dynamics in these materials is given elsewhere.[100, 101] More detailed reviews on layered halides with white emission can also be found in pervious reviews.[101, 102] Further investigations into this class of materials are needed to develop effective means to control the emissions and improve the PLQEs and stabilities, with which optically pumped WLEDs with higher performance would be possible.

### ii. One-Dimensional (1D) Organic Metal Halide Hybrids

One-dimensional (1D) organic metal halide hybrids are bulk assemblies of metal halide wires/chains/tubes made up of corner, edge or face sharing metal halide octahedra. In these materials, the 1D metal halides are isolated from each other by bulky organic cations, leading to strong quantum confinement in two dimensions. Our group reported the first luminescent 1D organic metal halide hybrid, $C_4N_2H_{14}PbBr_4$, in 2017,[103] which consists of metal halide wires made up of double edge-shared $PbBr_6^{4-}$ octahedrons surrounded by $C_4N_2H_{14}^{2+}$ cations (Figure 3g). It displays bluish white emissions peaked at 475 nm with a FWHM of 157 nm, and PLQEs of 20 % and 12 % for bulk and microscale crystals, respectively. The white emissions have CRIs of 63-66 and CCTs of 21,242 - 24,154 K. By doping $Mn^{2+}$ into this 1D organic metal halide hybrid, our group has improved the color quality of the white emissions with CRIs of up to 84 (Figure 3h).[104] Following our discovery of 1D $C_4N_2H_{14}PbBr_4$, many white emitting 1D organic metal halide hybrids have been developed and studied in the last couple of years. Peng et. al. developed a chiral white-emitting 1D metal halide hybrid based on double chains of highly distorted edge-sharing $PbCl_6^{4-}$ surrounded by $(C_5H_{13}N_2)^{2+}$ cations.[105] 1D $C_5H_{14}N_2PbCl_4{\cdot}H_2O$ displayed an excitation wavelength dependent broad white emission with a high CRI of 93.9, but a low PLQE of ~ 1%. Biswas et al. reported yellowish-white emitting 1D $(H_2O)(C_6H_8N_3)_2Pb_2Br_{10}$, with a structure composed of contorted corner-shared metal halide octahedra.[106] More recently, Paris and colleagues recently reported two broadband white emitting 1D organic metal halide hybrids based on $PbBr_6^{4-}$ octahedrons and different piperazine based organic cations.[107] Although the 1,4-bis(3-aminopropyl)piperazine (BAPP) based corrugated (110) 1D organic metal halide hybrid has a high CRI of 87, the PLQE is limited to 1.5%. In contrast, the trans-2,5-dimethylpiperazine (TDMP) based post-perovskite type 1D organic metal halide hybrid has a relatively low CRI of 75, but a record high PLQE of 45%. (Figure 3i)

The broadband emissions from 1D organic metal halide hybrids are attributed to self-trapped excitons due to strong exciton-phonon interactions, similar to those of 2D and corrugated-2D structures. Self-trapping in 1D organic metal halide hybrids is considered to be easier, as compared to 2D and corrugated 2D metal halide hybrids, because of the stronger quantum confinement and lower deformation energy required.[108] The choice of organic cation, halide anion and connectivity of the octahedrons are also believed to impact the self-trapping depth and PLQEs of 1D organic metal halide hybrids. While the recent developments of white emitting 1D organic metal halide hybrids are encouraging, rational design principles are still not available to guide the preparation of materials with high PLQEs needed for WLED applications. Moreover, device integration has not received much attention using these materials, which requires further exploration.

### iii. Zero-dimensional (0D) organic metal halide hybrids with broadband emissions

0D organic metal halide hybrids are ionically bonded materials, in which isolated metal halide photoactive species are periodically embedded in an organic matrix to form a perfect "host-guest" structure (Figure 4a).[109] Since 2017, our group has developed a series of highly luminescent 0D organic metal halide hybrids with tunable emission colors, by using various metal halides and organic cations.[110-113] For instance, 0D $(C_4N_2H_{14}Br)_4SnBr_6$,[111] $(Ph_4P)_2SbCl_5$,[113] and $(C_9NH_{20})_2SnBr_4$[112] have been prepared to exhibit yellow, orange, and deep red emissions with PLQEs of up to near-unity (Figure 4b). The photoluminescence mechanism of these materials, with no electronic band formation between individual metal halide species, could be explained in Figure 4c, i.e. strongly Stokes shifted emissions are observed from low energy distorted excited states after excited state structural reorganization.[111,114] Through structural and compositional control of these 0D organic metal halide hybrids, we have demonstrated emission color tuning spanning the whole visible spectrum (Figure 4d). All-inorganic 0D metal halides that display highly Stokes-shifted broadband emission have also been reported recently. For instance, Kovalenko's group synthesized $Cs_4SnBr_6$ all-inorganic 0D metal halide crystals with broadband room-temperature emission centered at 540 nm.[115] By varying both the A-site cation and halide component, they were able to demonstrate tunable emission with peaks in the range of 500 nm – 600 nm. Similarly, Su et al. reported a red emitting $Cs_2InBr_5 \cdot H_2O$ inorganic 0D metal halide with highly Stokes-shifted broadband emission and a PLQE of 33%.[116] Besides 0D organic metal halide hybrids containing mononuclear polyhedrons, our group has recently extended this 0D organic metal halide phase space to bulk assemblies of metal halide clusters, in which multiple metal halide polyhedrons are fused together to form multinuclear metal halide species. A particularly notable work is on the bulk assemblies of $[Pb_3Cl_{11}]^{5-}$ metal halide clusters. The optical emission from these clusters can be tuned from blue (peaked at 470 nm with a PLQE of ~ 83%) in $(bmpy)_7[PbCl_4][Pb_3Cl_{11}]$ (bmpy: 1-butyl-1-methylpyrrolidinium, $C_9NH_{20}^+$) to green (peaked at 512 nm with a near-unity PLQE) in $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ at room temperature, as a result of the change of crystal structure and surrounding molecular environment for $[Pb_3Cl_{11}]^{5-}$ species.[117, 118] Hosono et al. also reported bulk assembly of $[Cu_2I_5]^{3-}$ dimers that displays broad blue emission and a high PLQE of 90 %.[119]

The unique photophysical properties with highly efficient broadband emissions and little-to-no self-absorption, as well as good photostability of these 0D organic metal halide hybrids, make them of great interest for optically pumped WLEDs.[86] The first demonstration of WLEDs using 0D organic metal halide hybrids involved yellow emitting $(C_4N_2H_{14}Br)_4SnBr_6$ blended with a commercial blue emitting europium-doped barium magnesium aluminate ($BaMgAl_{10}O_{17}:Eu^{2+}$) in a polydimethylsiloxane (PDMS) matrix. By varying the relative concentration of the yellow and blue phosphors, the white emissions can be tuned with CCTs ranging between warm and cold. Balanced emissions between $(C_4N_2H_{14}Br)_4SnBr_6$ and $BaMgAl_{10}O_{17}:Eu^{2+}$ generated a white emission with CIE coordinates of (0.35, 0.39), a CCT of 4946 K and a 70 CRI. These WLEDs exhibited decent stability under varying operating current and ambient condition. Replacing $(C_4N_2H_{14}Br)_4SnBr_6$ by $(C_4N_2H_{14}Br)_4SnBr_xI_{6-x}$ (x =3), WLEDs with high CRIs of up to 85 have been demonstrated, as a result of increased coverage in the red spectral region.[120] Our group has also demonstrated a proof-of-concept WLED by combining red, yellow and green emitting 0D organic metal halide hybrids with the blue emitting commercial phosphor $BaMgAl_{10}O_{17}:Eu^{2+}$.[121] Several devices were fabricated by varying the ratio of the different phosphors to obtain white emission with CCT ranging from 3000 to 6000K (Figure 4e). Because of the broadband emission from the 0D organic metal halide hybrids, full coverage of the visible spectrum was easily achieved to mimic emission from a blackbody radiator. The champion device had CIE coordinates of (0.3782, 0.3722) with ultra-high CRI (99), CQS (99) and R9 (99) values (Figure 4f). The thermal stability of the devices was also tested for 96 hours at 85 °C and showed only a slight coordinate shift that does not exceed the industry standard. More recently, Xia et al. demonstrated a heterometallic 0D organic metal halide hybrid by incorporating multiple color centers in the form of anionic $[Pb_3Br_{11}]^{5-}$ clusters and $[MnBr_4]^{2-}$ tetrahedra. By coupling this 0D organic metal halide hybrid with a blue LED, WLEDs with CIE color coordinate of (0.319, 0.372), luminous efficiency of 80.93 lm/W , CRI of 79 and CCT of 6022 K were fabricated.[122]

0D organic metal halide hybrids are becoming the new rivals to the established phosphors because of their near unity PLQEs, color tunability, little to no self-absorption, simple wet-chemistry synthesis and broadband emissions with large FWHM. Moreover, most of the 0D metal halide hybrids reported to date are lead-free and based on earth abundant components. These easily prepared phosphors have the potential to enable the development of WLEDs with performances comparable or superior to commercially available lighting sources[38].

## IV. Double Perovskites

In search of lead-free, stable and efficient perovskite emitters, isovalent substitution of $Pb^{2+}$ by $Sn^{2+}$ and $Ge^{2+}$ has been explored. However, poor electronic and optical performances of lead-free isovalent metal ion substituted perovskites leave a lot to be desired. Instead, double perovskites, obtained through the heterovalent substitution of $Pb^{2+}$ by two metal ions (Figure 4g), have captured attention as an alternative route to lead-free perovskites. This class of materials has a general formula of $A_2BB'X_6$ (where A is a monovalent cation, B and B' are heterovalent metal ions and X is a halide ion) and can display broad emission from self-trapped excited states.

White emission based on lead-free perovskites was recently reported by Tang et al., where they prepared a lead-free double perovskite which exhibits efficient and stable white-light emission resulting from the Jahn–Teller distortion of the $AgCl_6$ octahedron in the excited state.[123] By optimizing the $Na^+$ content, the authors showed the highest ever reported PLQE (86± 5%) for a single white light emitting material (Figure 4h). The WLED based on optimally alloyed $Cs_2(Ag_{0.6}Na_{0.4})InCl_6$ with 0.04% bismuth doping has CIE coordinates (0.396, 0.448) with a CCT of 4,054 K, and negligible degradation when operated at about 5,000 cd $m^{-2}$ for over 1,000 hours in air (Figure 4i). The same group also demonstrated the colloidal synthesis of $Cs_2Ag_{1-x}Na_xIn_{1-y}Bi_yCl_6$ NCs. The resulting NCs showed emission color temperatures that can be tuned from 9759.7 to 4429.2 K by $Na^+$ and $Bi^{3+}$ incorporation.[124, 125] Although, white emitting double perovskites present a promising alternative to inorganic phosphors, their lack of absorption within the visible region limits their application to only UV LED based WLEDs, which show much lower device performance compared to those based on blue LEDs. Thorough studies by using double perovskites in optically pumped WLEDs are still lacking to date.

**Table 2:** Notable achievements in white light emission from metal halide perovskites and low-dimensional metal halide hybrids

| **Emitter** | ***Structure*** | **PLQE *(%)*** | **CIE** | **CRI/ CCT** | ***Luminous Efficiency (lm/W)*** | ***Ref.*** |
|---|---|---|---|---|---|---|
| **$CsPbX_3$** | 3D NCs | 50 - 81 | (0.312,0.333) | 96/ 6500 K | 62 | 60 |
| **$MAPbX_3$-$SiO_2$** | 3D NCs | 70 - 95 | (0.31,0.34) | 85/ 6581 K | 54 | 79 |
| **$Cs_2Ag_{0.6}Na_{0.4}InCl_6$** | Double perovskite | 86 | (0.33,0.32) | 90/ 4054 K | - | 123 |
| **$(2meptH_2)PbBr_4$** | 2D | 3.37 | (0.24,0.23) | 91/ - | - | 90 |
| **$(EDBE)PbBr_4$** | Corrugated 2D | 9, 18 | (0.39,0.42) | 84/ 3990 K | - | 87,93 |
| **$(TDMP)PbBr_4$** | 1D | 45 | - | 75/ - | - | 107 |
| **$(Ph_4P)_2MnBr_4$<br>$(C_4N_2H_{14}Br)_4SnBr_6$<br>$(Ph_4P)_2SbCl_5$** | 0D | 87 - 97 | (0.32, 0.33) | 99/ 5217 K | 9.73 | 121 |

## V. Summary and Outlook

Metal halide perovskites and low-dimensional metal halide hybrids have shown great promise as down conversion phosphors for optically pumped WLEDs. Thus far, perovskite NCs, double perovskites, and various types of low-dimensional metal halide hybrids have been demonstrated to possess desirable traits of ideal phosphors, such as high PLQE, good white light quality, and facile processability. However, there still remain many challenges to overcome before we can replace commercially successful inorganic phosphors with these emerging materials to achieve highly efficient optically pumped WLEDs with long lifetimes. Further research and development are needed to achieve ideal phosphors to meet all the following requirements. The raw materials used to synthesize the phosphors should be earth abundant, low cost, and eco-friendly; preparation of phosphors in high yield and low-cost energy efficient ways should be possible; the PLQEs should be as high as near-unity, the emissions should be highly tunable; the phosphors should have environmental, thermal and photo stability as good as conventional inorganic phosphors to ensure durability; and the integration of new phosphors into optically pumped WLEDs should be compatible with existing mass production processes. Moving forward, we expect that future efforts could be directed toward addressing the following issues.

- **Environmental, thermal and photo stability**: The stability of metal halide perovskites and low-dimensional metal halide hybrids still leaves a lot to be desired. This is partially because of the ionic nature of the crystal structures that have much lower formation energy and softer lattice than conventional covalently bonded inorganic materials. The use of various passivation and encapsulation techniques has been shown to reduce their degradation in the ambient atmosphere. Moreover, using all-inorganic perovskites has also proven to increase their thermal stability. Photostability of mixed halide perovskite NCs is another concern, as photoinduced ion migration has been shown to result in phase segregation and spectral instability. Further investigations are needed in the areas of nanocrystal passivation and ion migration suppression to make stable perovskite NCs suitable for optically pumped WLED applications. One promising approach to improving the stability is inorganic surface passivation of perovskite NCs. The success of inorganic core-shell quantum dots is a good example of how inorganic passivation can increase thermal and environmental stability. Moreover, unique device architectures such as remote phosphor WLEDs can mitigate thermal stress on perovskite phosphors.
- **Efficient lead-free perovskite NCs**: Thus far, perovskite NCs with near-unity PLQE have all been based on lead halide systems. However, the toxicity of these materials is a major concern that must be overcome before commercialization. The success in obtaining highly efficient lead-free double perovskites and 0D metal halide hybrids is encouraging. Besides traditional trial and error approaches, searching for lead-free metal halide perovskites with

direct band narrow emissions might be facilitated by computation supported combinatorial chemistry, in which screening of a large number of possible element combinations with tunable band structures could be realized.[126-128]

- **Emission tuning for better control of CRI and CCT**: One obstacle in using highly efficient perovskite NCs for optically pumped WLEDs stems from their narrow emissions. Although, the combination of blue, green and red emitting perovskite NCs can yield white emissions, the lack of full coverage of the visible spectrum leads to poor white light quality for lighting applications. The inclusion of multiple emitters to obtain good white light quality is also cumbersome. Broadband emissions from low-dimensional metal halide hybrids could possibly be more favorable for this reason. On the other hand, the gain in color quality through the use of broadband emitters presents efficiency tradeoffs due to spillover of light into the deep-red region. For this reason, a combination of a broad emission in the green-yellow region and a narrow red emission might be the best compromise to obtain good color quality as well as high luminous efficiency, when blue LEDs are used as the optical pump source.
- **Absorption of phosphors**: Because of the strong absorbance of metal halide perovskites and low-dimensional organic metal halide hybrids in the UV region, UV LEDs (365 nm) can serve as the common pump sources for down-conversion WLEDs. However, the low efficiency of UV LEDs, compared to blue LEDs, results in great efficiency loss. The use of more efficient near-UV and deep blue LEDs (for instance 405 nm) would address this problem but requires materials to have appropriate Stokes shifts and high absorption in this spectral region. So far, neither metal halide perovskites nor low dimensional metal halide hybrids have ideal Stokes shifts, i.e. the former too small with strong overlaps between absorption and emission resulting in cross/self-absorption energy losses, and the later too large with absorption band edges within the UV region. Future efforts could be directed toward visible light excitable materials with reasonable Stokes shift.
- **PLQE of low-dimensional organic metal halide hybrid white emitters**: Although low-dimensional organic metal halide hybrids with intrinsic white emissions show many advantages, such as large Stokes shift reducing re-absorption losses and size-independent optical properties, for use in optically pumped WLEDs, their PLQEs are still too low. There is still a lack of fundamental understanding of the radiative and non-radiative processes in

these materials. Also, no rational design principles are available yet to increase the PLQEs or control the broadband emissions of this class of materials. Detailed studies of the excited state structural and optical dynamics are therefore needed, which could be achieved by using ultrafast X-ray and optical spectroscopies.

- **Device engineering**: With the above issues on the material side being addressed, comprehensive device engineering studies with focuses on the suitability of various phosphor encapsulation techniques and device architectures would be necessary to bring the luminous efficiency of metal halide perovskite and low-dimensional organic metal halide hybrid based WLEDs up to par with the state-of-the-art WLEDs.

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## List of Figure Legends

**Figure 1:** Schematic illustrations of (a) the hot injection and (b) ligand assisted reprecipitation (LARP) methods.[40] Reproduced with permission from Chem. Rev. 119, 3296 (2019). Copyright 2019 American Chemical Society. (c, d) typical transmission electron microscopy (TEM) images of $CsPbBr_3$ NCs,[37] (e) colloidal solutions of $CsPbX_3$ under UV lamp (top) and representative PL

spectra (bottom).[37] Reproduced with permission from Nano Lett. 15, 3692 (2015). Copyright 2015 American Chemical Society. (f) emission tuning of $CsPbBr_3$ NCs with size reduction.[46] Reproduced with permission from ACS Energy Lett 3, 329 (2018). Copyright 2018 American Chemical Society.

**Figure 2:** (a) Schematic illustration of optically pumped WLEDs, (b) Electroluminescence (EL) spectra of a $CsPbX_3$-PMA WLED. The inset shows a photograph of the device in the measurement setup.[59] Reproduced with permission from ACS Appl Mater Inter 8, 19579 (2016). Copyright 2016 American Chemical Society. (c) EL spectra and six-color multipackage WLEDs obtained through halide mixing in $CsPbX_3$ (X = Cl, Br, I).[60] Reproduced with permission from ACS Appl Mater Inter 8, 18189 (2016). Copyright 2016 American Chemical Society. (d) EL spectra of the mixture of silica coated $CsPbBr_3$ and Mn doped $CsPb(Cl_{0.5}Br_{0.5})_3$. Inset shows a picture of the WLED in operation.[73] Reproduced with permission from ACS Appl Mater Inter 9, 40477 (2017). Copyright 2017 American Chemical Society. (e) Luminous efficiency of WLED based on alky phosphate coated $CsPbBr_3$ NCs measured in 60% RH in air for 15 hours.[74] Reproduced with permission from Nanoscale 9, 15286 (2017). Copyright 2017 Royal Society of Chemistry. (f) Photostabilities of $MAPbBr_3$ NCs and $MAPbBr_3$-NCs/$SiO_2$ powders.[82] Reproduced with permission from J. Am. Chem. Soc. 138, 5749 (2016). Copyright 2016 American Chemical Society.

**Figure 3:** (a) Crystal structure and (b) Photoluminescence emission spectrum of the corrugated 2D metal halide hybrid (EDBE)$PbBr_4$. Inset shows the crystal under UV irradiation.[92] Reproduced with permission from J. Am. Chem. Soc. 136, 1718 (2014). Copyright 2014 American Chemical Society. (c) Schematic of the adiabatic potential energy curves of the ground state (G), free-exciton state (FE), free-carrier state (FC), and various excited states (STEs) in a configuration space. The horizontal dashed line shows possible nonradiative decay processes of the STEs.[97] Reproduced with permission from J Phys Chem Lett 7, 2258 (2016). Copyright 2016 American Chemical Society. (d) Image of a UV-pumped white LED (operated at 3.0 V) by using microscale corrugated 2D perovskites as down conversion phosphors, (e) Emission spectra of the white-light LED demo at different operating voltages and (f) CIE coordinates for the white LED plotted on the CIE1931 chromaticity chart.[93] Reproduced with permission from Advanced Optical Materials 4, 2009

(2016). Copyright 2016 Wiley-VCH. (g) Crystal structure of the 1D metal halide hybrid $C_4N_2H_{14}PbBr_4$.[103] (h) Absorption (dashed line) and emission (solid line) spectra of the pristine and Mn-doped 1D lead bromide perovskites, the inset shows the images of the pristine and Mn-doped 1D lead bromide perovskites under ambient light (top) and UV light (365 nm, bottom).[104] Reproduced with permission from ACS Appl Mater Inter 9, 40446 (2017). Copyright 2017 American Chemical Society. (i) Crystal structure of post-perovskite-type chains $(TDMP)PbBr_4$. Inset shows the crystals under UV excitation.[107] Reproduced with permission from Adv. Mater. 31, 1807383 (2019). Copyright 2019 Wiley-VCH.

**Figure 4:** (a) Schematic drawing of a perfect host–guest system with the light emitting species periodically embedded in an inert matrix, (b) and its potential energy diagram.[111] Reproduced with permission from Chem Sci 9, 586 (2018). Copyright 2018 Royal Society of Chemistry. (b) Building block polyhedrons of 0D metal halide hybrids (top), representative crystals under ambient light (middle) and under UV excitation (bottom). (c) The mechanism of excited state structural reorganization: the straight and curved arrows represent optical and relaxation transitions, respectively.[111] Reproduced with permission from Chem Sci 9, 586 (2018). Copyright 2018 Royal Society of Chemistry. (d) Representative photoluminescence spectra of 0D metal halide hybrids and clusters. (e) White-light spectra based on 0D metal halide hybrids that mimics sunlight at different CCT.[121] (f) CRI comparison between YAG:Ce based WLED and champion WLED based on 0D metal halide hybrids.[121] Reproduced with permission from ACS Appl Mater Inter 10 (36), 30051 (2018). Copyright 2018 American Chemical Society. (g) Schematic illustration of $B^{+}/B^{3+}$ cation substitution from halide perovskites ($AB^{2+}X_3$) to double perovskites ($A_2B^{+}B^{3+}X_6$).[129] Reproduced with permission from J Mater Chem A 6, 1809 (2018). Copyright 2018 Royal Society of Chemistry. (h) Luminosity function (dashed line) and photoluminescence spectra (solid lines) of $Cs_2Ag_{0.60}Na_{0.40}InCl_6$ measured at different temperatures from 233 K to 343 K.[123] (i) Operational stability of $Cs_2Ag_{0.60}Na_{0.40}InCl_6$ down-conversion devices, measured in air without any encapsulation. The box plot shows the results for five different samples measured separately, with the box edges representing quartiles, the band inside the box showing the median and the end of the whiskers representing the minimum and maximum of the data. Inset shows a 300-nm-thick quartz substrate and 500-nm-thick $Cs_2Ag_{0.60}Na_{0.40}InCl_6$ films under 254-nm

ultraviolet illumination.[123] Reproduced with permission from Nature 563, 541 (2018). Copyright 2018 Nature Publishing Group.