

The Physics of Light Emission in Halide Perovskite Devices

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Light emission is a critical property that must be maximized and controlled to reach the performance limits in optoelectronic devices such as photovoltaic solar cells and light-emitting diodes. Halide perovskites are an exciting family of materials for these applications owing to uniquely promising attributes that favor strong luminescence in device structures. Herein, the current understanding of the physics of light emission in state-of-the-art metal-halide perovskite devices is presented. Photon generation and management, and how these can be further exploited in device structures, are discussed. Key processes involved in photoluminescence and electroluminescence in devices as well as recent efforts to reduce nonradiative losses in neat films and interfaces are discussed. Finally, pathways toward reaching device efficiency limits and how the unique properties of perovskites provide a tremendous opportunity to significantly disrupt both the power generation and lighting industries are outlined.

1. Introduction

Luminescence is a critical property that must be maximized to reach the theoretical limits of a variety of optoelectronic applications including photovoltaic solar cells (PVs) and photonic devices such as light-emitting diodes (LEDs) and lasers.^[1] In a PV device, any nonradiative recombination resulting from parasitic relaxation pathways of excited carriers will lead to smaller quasi-Fermi level splitting and, ultimately, lower open-circuit voltages.^[2] In an LED, maximizing the key figure of merit, the external quantum efficiency (EQE) of electroluminescence, requires high radiative efficiencies and efficient outcoupling of photons.

Metal-halide perovskites are generating enormous excitement for their use in high-performance devices owing to several promising attributes that favor strong luminescence in device structures.^[3,4] Polycrystalline perovskite thin films are processed by relatively crude self-assembly from solution

or vapor yielding moderately high defect densities compared to conventional semiconductors such as GaAs and Si. Nevertheless, they typically exhibit reasonable emission quantum efficiencies, suggesting a high tolerance to defects.^[5,6] Furthermore, they exhibit a remarkable response to a range of passivating post-treatments and additives, which has led to recent reports of internal luminescence quantum yields close to 100%.^[7–10] Recent reports of photon recycling, allowing multiple photon absorption and emission events for a given excitation,^[11,12] create opportunities to achieve high photon and charge-carrier densities in devices, as well as tailored photon management.

Here, we present our current understanding of the physics of light emission in state-of-the-art metal-halide perovskite

devices. We discuss the generation of photons, the management of photon incoupling and outcoupling, and how we could exploit these further in device structures. We discuss nonradiative recombination pathways and recent efforts to minimize such parasitic processes in neat films and interface structures, as well as key processes involved in photoluminescence (PL) and electroluminescence (EL) in devices. Finally, we outline pathways toward reaching device efficiency limits and how their unique properties provide a tremendous opportunity to achieve PV and LED performances beyond those of existing commercial technologies.

2. State-of-the-Art Devices

The recent rise of halide perovskite optoelectronics was initially driven by rapid empirical improvements in solar cell power-conversion efficiency (PCE). The improvements in both performance (current certified record PCE of 22.7%)^[13] and stability since the initial reports in the period 2009–2012^[14] have been driven by three key factors. First, a realization that the perovskite itself could both absorb light strongly and efficiently transport charges, leading to simple planar heterojunction solar cell configurations in which the perovskite layer is sandwiched between charge-collecting contacts.^[15] Second, rapid improvements in crystalline film quality and homogeneity through new, primarily solution-based deposition routes.^[16] Third, an evolution of the composition from MAPbI₃ toward alloyed configurations in which fractions of the MA are replaced with formamidinium (FA) and/or cesium, and fractions of the iodide are replaced with bromide.^[17,18] The state-of-the-art configuration is a combination of each of these factors,^[13,18] with devices consisting of very thin mesoporous scaffolds but predominantly bulk perovskite in the

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active layer of an alloyed composition such as $(\text{Cs}_{0.06}\text{MA}_{0.15}\text{FA}_{0.79})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$. Recent passivation approaches with alkali halides such as KI and RbI have pushed device voltage losses from the radiative limit to as low as 0.11 V,^[8,19] yet these losses are still greater than those in GaAs (≈ 0.04 V).^[20]

In parallel, halide perovskite LEDs (PeLEDs) have emerged as an important area of scientific research since the first report in 2014.^[21] Early-stage developments focused on “bulk” halide perovskite emitters such as methylammonium lead halides, showing electroluminescence EQEs on the order of 1%.^[21] Initial rationales for efficiency improvements included morphological control and charge confinement through halide perovskite nanocrystals.^[22,23] Interfacial modifications to enhance charge injection and balance have also proven to be a useful strategy.^[24] A combination of these methods led to EQEs exceeding 8%.^[25,26] Recently, quasi-2D/3D perovskite structures were shown to be effective in improving EQEs to $\approx 14\%$.^[27–29] These structures lead to a build-up of charge carriers in the lower-bandgap regions of the emissive material, which helps overcoming nonradiative recombination losses. We refer the reader to references discussing appropriate means to measure PV and LED devices.^[30]

3. General Luminescence Considerations

Metal-halide perovskite thin films show a sharp absorption onset (Figure 1a),^[3,31–33] with low Urbach energies (≈ 13 meV)^[34] that are comparable to other high-quality semiconductors (7.5 meV GaAs, 9.6 meV for c-Si).^[35] The luminescence is sharp and near the band edge (Figure 1a), with the linewidth dictated by homogeneous broadening due to phonon coupling effects.^[36] These properties suggest that they are relatively clean semiconductors with low levels of energetic disorder even in spite of a moderately large defect density.

A schematic of a typical PeLED stack is shown in Figure 1b, where the emitting perovskite layer is sandwiched between electron-injecting (ZnO/PEIE) and hole-injecting (TFB) contacts. Under operation, charge carriers (electrons and holes) enter the two terminals of the device by drift under an external field. Electroluminescence occurs when the oppositely charged carriers recombine radiatively in the semiconducting perovskite layer. This typically occurs via band-to-band carrier recombination

or via exciton formation and relaxation. Several conditions are required for efficient EL: 1) the net ratio of electron and hole injection currents in the diode should be maintained to be as close to unity as possible (charge balance); 2) the probability of carriers leaving the diode without recombining should be minimized (leakage current); 3) the ratio of radiative to nonradiative recombination events should be maximized (high luminescence quantum efficiency); 4) the photons generated within the emissive layer should be efficiently extracted (outcoupling). The external quantum efficiency of EL for an LED can be described by Equation (1):

$$\text{EQE} = f_{\text{balance}} \times f_{\text{e-h}} \times \eta_{\text{radiative}} \times f_{\text{outcoupling}} \quad (1)$$

where f_{balance} is the probability of balanced charge injection (when the numbers of electrons and holes injected are equal, this factor is equal to 1), $f_{\text{e-h}}$ is the probability of forming a correlated electron–hole pair or exciton from each pair of injected carriers, $\eta_{\text{radiative}}$ is the probability of radiative recombination for each electron–hole pair, and $f_{\text{outcoupling}}$ is the optical outcoupling coefficient.

Achieving high external EL efficiency is also critical for solar cells as nonradiative recombination is a major source of voltage and efficiency losses.^[37] The open-circuit voltage of a solar cell V_{OC} is related to the device acting as an LED by

$$V_{\text{OC}} = V_{\text{OC}}^{\text{max}} - \frac{kT}{q} \ln[\eta_{\text{LED}}] \quad (2)$$

where $V_{\text{OC}}^{\text{max}}$ is the maximum achievable voltage after unavoidable thermodynamic and entropic losses (i.e., the radiative limit), T is the temperature, k is the Boltzmann constant, and q is the charge of an electron. Indeed, there is an empirical positive correlation between the external radiative efficiency of a PV device and the power conversion efficiency.^[38]

4. Photon Generation in Halide Perovskites

The initial step for light emission is the formation of an emissive state from optically injected (cf. PL) or electrically injected (cf. EL) excited states/charges, from which the emission of a photon occurs. Efficient light emission requires

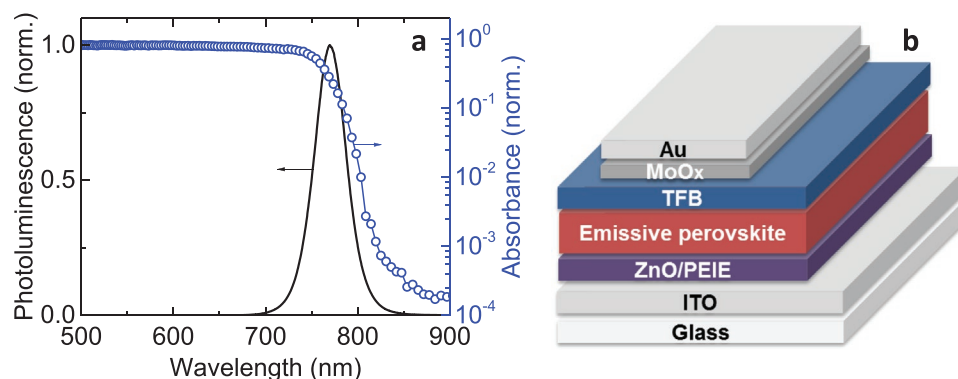


Figure 1. a) Photoluminescence spectrum (left axis) and absorption spectrum as measured by photothermal deflection spectroscopy (PDS, right axis) of a $(\text{Cs}_{0.06}\text{MA}_{0.15}\text{FA}_{0.79})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ thin film. b) Schematic of a typical PeLED device stack with an emissive perovskite sandwiched between an electron injector (ZnO/PEIE) and a hole injector (TFB). Adapted with permission.^[28] Copyright 2016, Macmillan Publishers Limited.

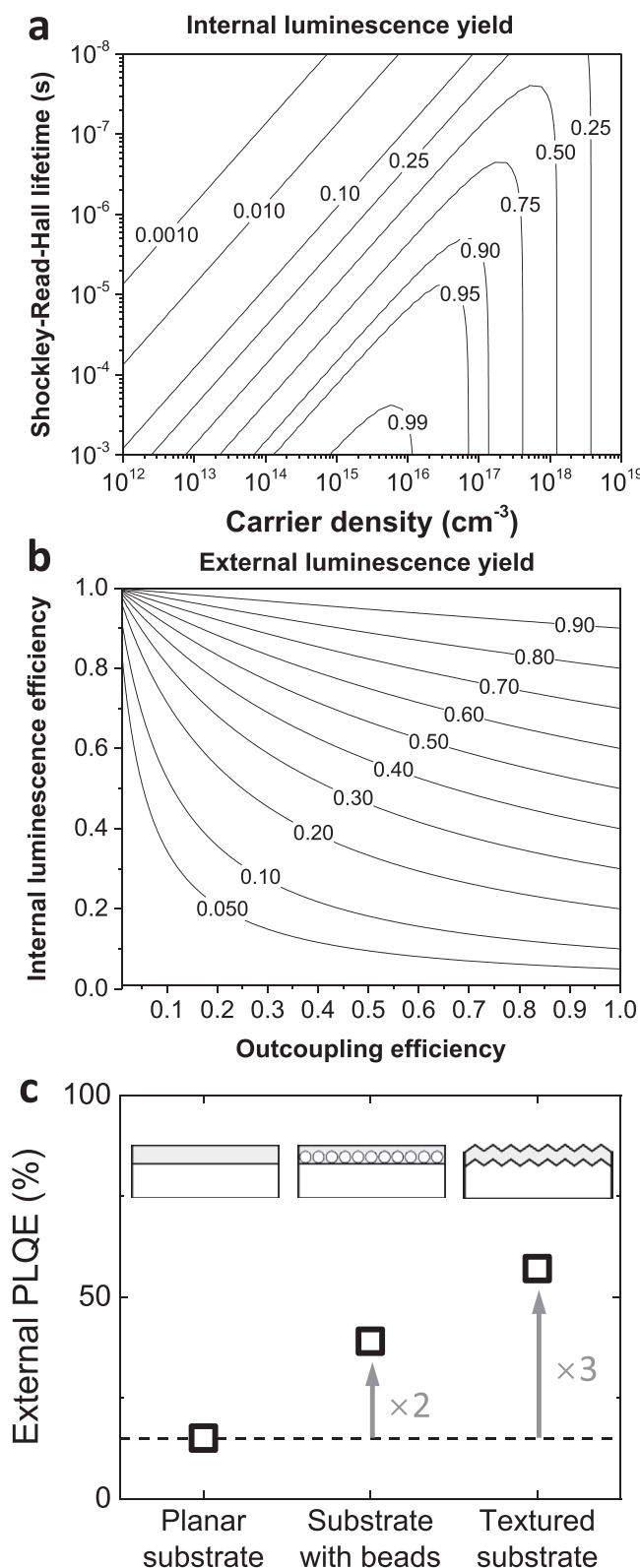


Figure 2. a) Calculated internal luminescence yields as a function of carrier density and extrinsic Shockley–Read–Hall lifetime using reported values for bimolecular ($1.35 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and Auger ($1.1 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$) recombination constants.^[12,56] b) External luminescence yields as a function of outcoupling efficiency and internal luminescence yield calculated by

injected or photoexcited charges to interact strongly regardless of whether the recombination arises from free carriers or excitonic states. It is well understood that the large dielectric constants in bulk halide perovskites lead to low exciton binding energies,^[39,40] and that radiative recombination is dominated by unexpectedly efficient free charge-carrier recombination.^[7,41] This process depends quadratically on carrier density, which makes charge capture the limiting step for radiative, bimolecular recombination events in bulk halide perovskite. The intrinsic bimolecular recombination constant is determined by the electron and hole interaction cross-sections and group velocities. Together with nonradiative Shockley–Read–Hall (SRH) recombination, which depends on the trap densities in the material and, as such, is an extrinsic property, the combination of these recombination pathways leads to internal luminescent yields that are strongly dependent on the carrier density in the emitter layer (**Figure 2a**). Values for the material-specific recombination constants can be extracted by transient spectroscopy.^[12,42,43] We note that transient luminescence measurements are typically conducted at low excitation densities at which monomolecular processes dominate the charge population decay kinetics,^[44,45] while bimolecular processes are better accessed at higher excitation densities available from amplifier laser systems.^[7,12,43]

The interplay between the different recombination mechanisms predicts that the highest internal luminescence yields occur for carrier densities in the range of 10^{15} – 10^{17} cm^{-3} . At higher carrier densities, Auger recombination reduces luminescence yields. Obtaining high luminescence yields below carrier densities of 10^{13} cm^{-3} will require extremely low nonradiative recombination rates (equivalent to carrier lifetimes in the range of milliseconds at these low carrier densities) unless methods are found to dope the halide perovskite emitter layer to increase the radiative rates of minority carriers.^[46] For PeLEDs, the challenge to achieve high luminescence rates for low carrier densities has been tackled using very thin emitter layers,^[21] carrier funneling and concentration to local recombination sites,^[27] and inclusion of lower-dimensional halide perovskites, in which spatial confinement forms states with strong excitonic nature that are not limited by carrier density-dependent rates.^[23,47] However, disrupting the bulk crystal structure is likely to lower charge transport rates. The control of carrier interactions and recombination through tailored dielectric screening within the bulk perovskite lattice, for example by using moieties with varying polarity, could offer future gains since the interactions between charges could be increased without affecting the bulk crystal structure required for charge transport. Despite this mechanistic consideration, the exact nature of charge carriers and their interactions is not fully understood. It is currently debated how the soft nature of the lattice interacts with charges, and effects from photo-induced ion motion are expected to change local dielectric

considering photon-recycling processes. c) Demonstration of improved external luminescence yields in MAPbBr₃ thin films on micropatterned substrates. c) Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International License.^[12] Copyright 2017, The Authors, published by Springer Nature.

potentials,^[48] which control the strength of carrier interactions. Further investigation of these questions is required to fully unravel the effects on charge-carrier recombination. Further, based on the strong spin-orbit coupling in halide perovskites, Rashba-type band splitting has been proposed to delay the recombination of charge carriers.^[49] In line with this, recent circular photogalvanic effect measurements have hinted at phototransport in spin-split bands.^[50] However, the bimolecular recombination rates in halide perovskites match predictions from absorption coefficients and are of comparable magnitude to the reported second-order recombination constants for III–V semiconductors without Rashba effects (both are in the order of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$).^[12,51] Furthermore, the luminescence is not thermally activated.^[52] These seemingly contradictory results could be rationalized by considering dynamics of the lattice or carrier localization effects. For conclusive answers, measurements of the dependence of the bimolecular recombination constant on carrier temperature, more direct probes of Rashba-type effects^[53] or insights into the halide perovskite structural dynamics after photoexcitation, will be required.

5. Light Outcoupling and Photon Recycling

Outcoupling of generated photons is a central process for light-emitting diodes.^[54,55] Importantly, it also controls the efficiencies of solar cells by setting the internal photon densities that define the open circuit voltage.^[1,2,56] The outcoupling efficiencies of photons generated in the active area are defined by the optical constants of the material, which are described by the real and imaginary parts of the dielectric function. The most relevant physical effects are reflections at the interface between the photoactive material and the material into which the photons are emitted, as well as self-absorption. The halide perovskite's optical constants have been determined experimentally from measurements of the refractive index and absorption spectrum, with relative refractive indices reported to be ≈ 2.5 for MAPbI₃.^[32,39,57] These values have been measured without photoexcitation, and for uncontacted films on glass, but the ionic nature of the halide perovskite materials, and the soft nature of the crystal structure, make it likely that photogeneration of charges affects the dielectric functions through structural and compositional changes.^[58] Similar effects are likely for current injection, and it remains to be understood how the refractive index changes under device operation.

In materials with high luminescence efficiencies and inefficient light outcoupling, photon recycling will occur.^[59] In this process, a fraction of the photons that are generated in the active layer is reabsorbed before leaving the device, which then creates “recycled” photon emission. Therefore, a second crucial aspect of light outcoupling that dictates the prominence of photon recycling is the energetic alignment of absorption and emission profiles. Measurements of the absorption spectra of halide perovskites, which probe the imaginary part of the dielectric function, are available with high sensitivity.^[32,33,60] These show a sharp absorption onset (cf. Figure 1a) that is convoluted with a weak excitonic peak due to the low exciton binding energies. The exact shape of the halide perovskite

absorption onset further depends on many things, including, among others, the halide perovskite composition, lattice dimensionality, the energy and spatial distributions of defects, grain size, and film nanostructure. The shape and energetic alignment of absorption and emission levels control the photon reabsorption in the active layer, which is a parasitic loss in materials with low luminescence quantum efficiency. In organic LED (OLED) devices, this problem typically is not very relevant because the emission is sufficiently redshifted relative to the absorption profile. In the hybrid perovskites, the absorption onset is exceptionally sharp, but reaches very high levels ($>10^4 \text{ cm}^{-1}$) at energies above the absorption edge. Since the PL is only very slightly shifted against the absorption (Figure 1a), strong reabsorption of generated photons occurs. Based on these reported properties for the optical constants of MAPbI₃, the outcoupling efficiency for this halide perovskite has been calculated to be 6.7% for a flat film on glass,^[56] which sets the upper limit for the maximum external quantum yields that can be achieved in hybrid perovskites in the absence of photon recycling or scattering.

Photon recycling allows for multiple outcoupling events to occur in the halide perovskites and may explain the many reported external photoluminescence quantum efficiencies (PLQEs) exceeding the outcoupling limit of 6.7%, highlighting the relevance of photon recycling for the luminescence of halide perovskites. Even without detailed knowledge about the dynamics of the recycling process, one can model the effect of photon recycling on the external luminescence yields taking into account the material's internal luminescence yields and its outcoupling efficiencies^[12] (Figure 2a,b). To achieve external luminescence yields exceeding 20%, the outcoupling efficiency of a flat halide perovskite film requires internal luminescence yields to exceed 80%. On the other hand, by increasing the outcoupling efficiency by a factor of 5, for example through surface structuring, the value for the internal luminescence to exhibit the same external yield drops below 40%. The viability of this approach has been successfully demonstrated from a threefold increase in external luminescence yields in microstructured MAPbBr₃ thin films (Figure 2c).^[12]

6. Factors Limiting Performance in Devices

6.1. Photoluminescence (PLQE) and Electroluminescence Quantum Efficiency (ELQE)

PLQE and ELQE are both key quantities to assess radiative efficiency in films and devices, with both depending on carrier density.^[61] In devices, particular care is required to distinguish between intrinsic material quantities and extrinsic quantities that are affected by sample properties (e.g., thickness, architecture) and measurement (e.g., detection geometry) properties.^[12] Although it may seem trivial, it is necessary to clarify that several important differences exist between PL and EL, so that the discrepancy between PLQE and ELQE can be understood. In contrast to the EL processes, PL proceeds through initial photoexcitation (typically above the bandgap) followed by rapid relaxation to near the band edges of the semiconductor.

So, what causes EL and PL to have different quantum efficiencies in nonideal devices? The first reason is the potential charge imbalance in the EL process. Due to the nature of the photoexcitation process (as in PL), the electrons and holes are created simultaneously upon photon absorption. The local ratio between the two carriers immediately after excitation approaches 1:1. Under EL conditions, there can be spatial imbalances in electron and hole densities in the active layer upon electrical injection from electrodes at opposite sides of the active layer. The carriers that have opportunities to recombine are those that are captured by the local electrostatic potential (e.g., in quantum well structures) or by the charge-blocking layers. Second, under electrical excitation, the injected charges (and the excitations they later form) preferentially occupy sites with lower energies. In contrast, all possible states accessible by the energies of the incoming photons are excited simultaneously under photoexcitation. This could be particularly relevant for the quasi-2D/3D structures that have considerably more energetic subgap broadening than their pure 3D counterparts. Third, one or both processes (PL and EL) may be influenced by additional factors such as spin and angular momentum of the excitation, with photon emission from states (cf. triplet states in OLEDs) that require a change in momentum to relax to the ground state normally prohibited, reducing the maximum EL efficiency.

6.2. Nonradiative Recombination Mechanisms in Neat Films and Interfaces

Typical external PLQE values of perovskite bulk thin films such as MAPbI₃ or (Cs,FA,MA)Pb(I_{0.85}Br_{0.15})₃ under illumination intensities comparable to 1 sun are on the order of 1–10%, which translates to internal PLQE values typically <50%^[5,7,8] (cf. Figure 2b). These values increase with higher carrier density yet internal values still plateau well below 100%. This is consistent with a nonnegligible density of subgap states (typically $\approx 10^{13}$ – 10^{15} cm⁻³ in polycrystalline films^[7,42,43]) that dominate the nonradiative, monomolecular recombination and set the values for the SRH recombination constants in Figure 2a. These states can be saturated at carrier densities beyond the trap densities in which case recombination is primarily radiative and bimolecular.^[7,12,51] The trap densities are spatially heterogeneous, with sizeable differences grain to grain when luminescence is visualized on the microscale.^[62,63]

Although many defects in halide perovskites result in shallow trap states^[64] or states that lie within the bands, providing at least in part an explanation for the apparent defect tolerance, the substantial nonradiative losses present in these structures suggests there is still a density of deeper states.^[65] The specific origin of these trap states is still unclear but it is likely that halide vacancies, particularly at the grain boundaries and surfaces, are playing a key role.^[8,10] This proposition is further evidenced by recent discoveries of approaches that can effectively mitigate nonradiative decay by passivating or removing these defects. Recently, we showed that the addition of potassium iodide to the precursor solutions increased the internal PLQE of the resulting films to over 95%.^[8] The KI

acts to manage halides: it acts as both a source of halide, filling halide vacancies, but also immobilizes the excess halide into benign potassium species. Indeed, recent record-performing perovskite PV devices have been achieved through compositional halide management.^[13] Chemical passivation approaches have also been utilized in which post-treatments with Lewis bases such as pyridine and tri-*n*-octylphosphine oxide (TOPO) have significantly increased the PLQE and PL lifetime, with the latter treatment leading to carrier lifetimes in excess of 8 μ s and internal PLQE exceeding 90% for MAPbI₃ films, with similar improvements for quasi-2D films.^[9,29,62,66,67] Here, it is proposed that the electron-donating moieties bind to the uncoordinated lead sites arising from halide vacancies.^[66,67] We and others have shown that illuminating the films or crystals in the presence of atmospheric molecules can lead to substantial increases in the PLQE and PL lifetimes, with internal PLQE again exceeding 90%.^[10,68,69] Here, it has been proposed that oxygen is able to bind strongly to surface halide vacancies and, in the presence of photoexcited electrons, forms superoxide, which is effective at passivating the vacancy sites.^[69,70]

Similarly high PLQE values are reported in perovskite nanocrystal structures such as CsPbX₃, in which a combination of charge confinement and surface passivation with ligands yields external PL quantum efficiencies >90%. It is important to also note here that outcoupling can reach values close to 100% in nanosized structures with dimensions below the emission wavelength. Layered 2D and quasi-2D structures including nanoplatelets can achieve reasonable emission yields through similar arguments and could reach external PLQEs as high as their quantum dot counterparts.^[71]

Although the PLQE and PL lifetime of a film on glass or quartz substrates is an important quantity, a more relevant quantity to assess its performance in a device is when the material is interfaced with device electrodes. These contacts are likely to introduce additional nonradiative decay pathways through interfacial defects^[5,72] as well as additional constraints on photon in- and outcoupling. A device with ideal contacts would not introduce any reduction in PLQE or quenching of the carrier lifetimes; indeed, at open circuit, all recombination should be radiative and occur in the perovskite layer itself. In Figure 3a, we show that a neat (Cs,FA,MA)Pb(I_{0.85}Br_{0.15})₃ film on glass has an external PLQE of $\approx 20\%$, but when it is interfaced with typical solar cell n-type (TiO₂) and p-type (Spiro-OMeTAD) contacts this value drops to $\approx 1\%$.^[8] By adding passivating potassium halide additives, which decorate the grain boundaries and interfaces, this loss is substantially reduced, with the PLQE of the full device stack retained at $\approx 15\%$ and reduced open-circuit voltage loss from the radiative limits (0.11 V) much lower than the unpassivated case (0.26 V).^[8] This is also seen in retention of longer PL lifetimes with the potassium passivation even in the full solar cell device stack (Figure 3b). PeLEDs with quenching TiO₂/spiro-OMeTAD electrodes exhibit low external quantum efficiencies, despite high external PLQEs in the neat film on a nonquenching substrate,^[19,21,73] which agrees with the presence of extra losses at the interfaces.

Nonradiative interfacial losses have been reduced through the use of thin, insulating polymers between the injector and perovskite, e.g., polystyrene^[74] and polyvinyl pyrrolidone (PVP).^[75] It has been shown that the use of PVP between the

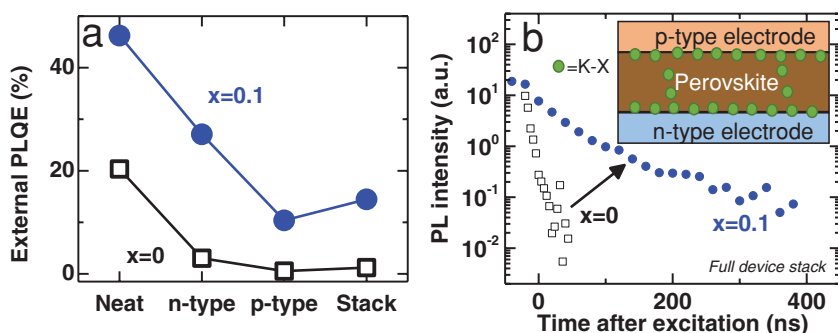


Figure 3. a) External PLQE of $(\text{Cs,FA,MA})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ perovskite thin films with 0% and 10% KI (x) added, measured under 60 mW cm^{-2} with a 532 nm CW laser ($\approx 1 \text{ sun}$). b) PL decays of the same perovskite films sandwiched between standard n-type (TiO_2) and p-type (Spiro-OMeTAD) solar cell electrodes. Adapted with permission.^[8] Copyright 2018, Macmillan Publishers Limited.

ZnO electron injector and $\text{Cs}_{0.87}\text{MA}_{0.13}\text{PbBr}_3$ perovskite emitter improves the PL intensity by a factor of ≈ 5 , with the external PLQE of the emitter reaching 55% on PVP and the EQE of the LED device increasing to 10.4%.^[75] Amine interfacial layers (e.g., polyethylenimine^[24] and ethylenediamine^[76]) have also been shown to improve the external PLQE of neat films and the EQE of the resulting LEDs. These improvements were attributed to the nitrogen atoms from the amine bonding with undercoordinated lead ions^[76] and reducing the density of recombination centers in the films. Similar mechanisms have been proposed for passivation by TOPO^[66] and other Lewis bases such as pyridine.^[67] In each of these approaches, there may be a necessary compromise between improved passivation and potential charge injection barriers.

6.3. Charge Injection and Balance in LEDs

Charge balance in an LED is influenced by the injection efficiency for electrons and holes. This depends on the energy barrier between the electron (hole) injector and the conduction (valence) band of the perovskite. For visible-light emitting perovskites, the lower electron affinities and higher ionization potentials that result from the wider bandgap result in larger injection barriers with conventional charge transport materials (e.g., ZnO or PEDOT:PSS). The electron injection efficiency has been improved by lowering the electron affinity of the electron injector (e.g., by alloying ZnO with Mg^[77]) or by using an interfacial layer between the injector and emitter (e.g., polyethylenimine^[24]). Similarly, to reduce the hole injection barrier, the hole injection level has been increased through doping (e.g., by adding a perfluorinated ionomer or MoO_3 into PEDOT:PSS^[78]) or by substitution with a higher-HOMO hole injector (e.g., 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl or CBP^[79]). Further details of efforts to tune injection barriers are given in ref. [80].

The injection barrier is typically determined by measuring the band positions of individual layers in the device through photoemission spectroscopy. However, the band positions of the perovskite layer are influenced by the work function of the substrate and care needs to be taken to perform photoemission spectroscopy of the perovskite deposited on the precise

substrate used in the device.^[81] Another approach is to use electroabsorption spectroscopy to measure the injection barriers present in a device stack.^[82,83] In electroabsorption spectroscopy, the effect of an internal electric field on the transmittance is measured. According to one-electron Franz-Keldysh-Aspnes (FKA) low-field theory, the change in transmittance depends on the square of the applied electric field,^[84,85] and this has been found to be applicable to MAPbI_3 and other bulk semiconductors.^[85] Modulating the internal electric field with a DC bias allows the internal field to be measured;^[83,86] however, the impact of ionic screening must be carefully considered.

7. Opportunities to Move beyond Existing Technologies

7.1. High-Brightness Operation

An important advantage of perovskite LEDs is their potential to operate under ultrahigh-brightness conditions similar to what can be achieved in conventional inorganic LEDs. This is partly because halide perovskite thin films have reasonable carrier mobilities on the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with relatively balanced bipolar charge transport.^[44,87] This can allow high currents (on the order of 100 mA cm^{-2} or higher) to flow through the diode without causing detrimental processes such as excessive heating and charge accumulation, offering possible advantages over organic and colloidal quantum-dot semiconductors for high-brightness operation. Peak luminance exceeding 10^5 cd m^{-2} has been achieved^[75] and a recent encouraging report of LEDs utilizing 2D perovskites showed operation without considerable droop at current densities on order A cm^{-2} .^[88] However, high-brightness operation in perovskite LEDs is currently hindered by other factors including the instability of the ionic material under electric field (ion migration),^[89] unbalanced carrier injection, as well as nonradiative and Auger recombination losses which occur predominantly under low/high injection conditions, respectively,^[90] and may further contribute to heating-related degradation.

7.2. Photon Management in LEDs and Solar Cells

While the internal luminescence yields of the perovskites are yet to approach their full potential, large gains are possible from outcoupling approaches, in particular for LED efficiencies. Management of the emitted photon flux is an established approach in other LED technologies.^[55] The required multi-layer architecture in operating devices introduces additional outcoupling challenges, but also opportunities due to the electric field distribution in the active layer.

To improve photon extraction in PeLEDs, several general strategies are considered. First, significant optical losses in lateral waveguided substrate modes can be minimized by

introducing patterned structures with appropriate refractive indices on the air-side of the glass substrate. Such approaches have been shown to lead to outcoupling enhancements of up to twofolds^[91] for OLEDs. Second, a simpler alternative to the above strategy is the use of index-matched substrates and outcoupling films which improves light coupling by increasing the photon escape cone without altering the shape of the substrate surface. This method provides additional advantages for display applications that require nonscattering surfaces. Third, the application of microcavity or photonic structures such as distributed Bragg reflectors (DBRs)^[92] in the LED structure alters the spatial and spectral distribution of the electromagnetic field in the device structure, leading to potential enhancements in the outcoupling efficiency. This offers opportunities to use imbalances in charge distribution profiles over the active area, for example through control of charge transport and injection, to steer the position of the emission layer in the active material to enhance outcoupling efficiencies. The fourth option is the enhancement of optical scattering via the use of nanostructures in any layer of the device stack^[93] provided they can be efficiently contacted. Recent reports of nanodot-in-matrix structures highlight the viability of this approach.^[25,94]

Photon management is also critical for reaching the efficiency limits in a solar cell. One strategy to reach the highest open-circuit voltage is to maximize the photon and charge-carrier densities in the absorber material. The capability of perovskites to efficiently recycle photons with low loss (high internal luminescence yield) facilitates high carrier densities and therefore large quasi-Fermi Level splitting. Indeed, strong photon recycling is widely viewed to be a critical factor in GaAs achieving such a low open-circuit voltage loss.^[2] Such performance improvements with photon management can be considered to be a similar approach to concentrated photovoltaics; a recent study suggested that, based on charge-carrier recombination and extraction rates in the devices, halide perovskite performances will substantially benefit from solar concentration.^[95] Counter-intuitively, efficient photon outcoupling is also important in a solar cell. In order to minimize entropic losses, one would ideally design the solar cell such that all of the radiative recombination is emitted into a narrow cone back in the direction of the sun with a very high external luminescence yield,^[2] although in practice this is harder to achieve.

7.3. PeLEDs versus OLEDs

Based on realistic device architectures modified from a recent work,^[28] a theoretical EQE limit of $\approx 20\%$ in the forward direction of the planar LED structure can be calculated by assuming 100% IQE in the emissive layer and using optical models similar to those used for planar OLEDs (unpublished results). In the OLED model in which photon recycling is negligible because of minimal overlap between absorption and emission, light is predominantly wave-guided laterally; in materials where photon recycling is significant, more of the light can instead be emitted in the forward direction out of the device (**Figure 4**). By taking photon recycling effects into consideration, a very optimistic estimate of the EQE limit for

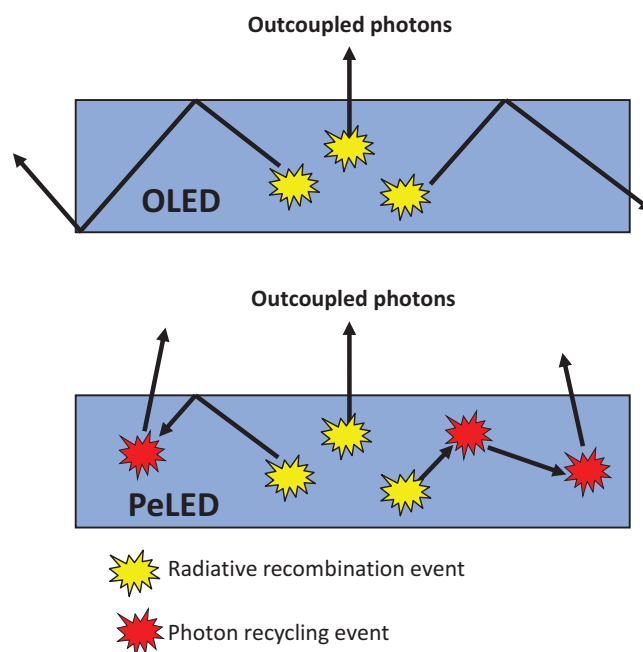


Figure 4. Simplified schematic to compare the light outcoupling in an OLED (top) and PeLED (bottom), with the arrows denoting photon trajectories. In an OLED, the large redshift of the emission peak from the absorption onset (Stokes shift) means there is negligible reabsorption and hence minimal photon recycling. Therefore, a large fraction of the photons is waveguided laterally in the film and thus the outcoupling in the forward direction is limited to 20–30% in a system with 100% internal quantum efficiency. In a PeLED, photon recycling events are prominent due to the significant overlap between absorption and emission. This means a larger fraction of the waveguided photons have the opportunity to be remitted and outcoupled in the forward direction.

the LED structure is $\approx 75\%$, as such effects are in principle useful in extracting the trapped optical modes from the perovskite layer. Here, the fractional optical power is assumed to be up to $\approx 55\%$, which refers to the ratio of the power of a given optical mode (e.g., waveguided photons) in the LED structure to the total (maximum) optical power of the photon source in the emissive layer. It should be emphasized that reaching this efficiency level requires an IQE of very close to 100%, which assumes complete elimination of nonradiative losses. Another challenge for fully utilizing the effect of photon recycling is that the isotropic reabsorption/re-emission processes can induce depolarization of the polarized light required to minimize contrast loss due to reflections. This depolarization effect is undesirable for LED display applications and therefore a trade-off may exist between EL efficiency and image clarity.

Overall, compared with conventional OLEDs, perovskite LEDs arguably offer several potential advantages: 1) as discussed earlier, the excellent charge transport properties of halide perovskites allow for higher brightness to be achieved at relatively low driving voltages. These also lead to improved power efficiencies; 2) the color purity of perovskite LEDs, typically characterized by the spectral narrowness of the EL, is superior to most of the high-efficiency OLEDs. Typical FWHM of the EL spectra from perovskite LEDs^[21,25] and OLEDs^[96] are 20–30 and 50–100 nm, respectively. 3) Due to the broad bandgap tunability of perovskite emitters in the visible spectrum,^[97] they offer prospects

to achieve a wider color gamut. 4) The design flexibility for achieving high-efficiency perovskite LEDs is greater than that for OLEDs, thanks to the relatively small electron–hole binding energy and the strong spin–orbit interactions in the hybrid perovskite materials.^[98] In OLEDs where the electron–hole pairs exist in the form of excitons, high EL efficiencies have been hindered by spin statistics which renders spin-triplet excitons nonemissive, leading to an IQE limit of 25% for conventional electrofluorescence. Materials and mechanisms for surpassing this limitation, including phosphorescence^[99] and delayed fluorescence via reverse intersystem crossing^[96] or triplet fusion,^[100] have been extensively explored in the past decades. In particular, electrophosphorescence has been widely used in commercial OLEDs. However, these approaches typically require specialized molecular design and synthetic procedures. PeLEDs are not limited by such design considerations due to the reduced excitonic nature of carrier interactions.^[31,40,98]

While OLED displays have emerged to become a major industry worldwide, perovskite LEDs are still very far from practical applications mainly due to issues including toxicity associated with lead (discussed below), reproducibility and operational stability that must be resolved. Moreover, the EL efficiencies of perovskite LEDs, with maximum EQEs of around 14% reported,^[29] are still low compared to state-of-the-art OLEDs.^[96] Difficulties in developing reliable and high-throughput solution processing methods that rival vacuum-deposited OLED technology hinder further development. If these drawbacks can be fully overcome, perovskite LEDs are likely to complement or challenge the position of OLEDs in commercial applications.

7.4. Lead-Free Emitters

Owing to their rapidly rising performance, halide perovskite emitters are a promising alternative to cadmium-based quantum dot emitters. Halide perovskites can replicate the highly desired properties of quantum dots for display applications, such as sharp electroluminescence and solution processability.^[101] Cadmium-free emitters for display and lighting products are important because European regulations restrict the cadmium content in electronic products to 0.01 wt%, and the previous exemption for quantum dot displays is due to expire in 2019.^[102] However, the same regulations also restrict the lead content in electronic products to 0.1 wt%, which is exceeded in Pb-based perovskites (36 wt% Pb in MAPbI₃).^[103] we note that there are exemptions for PV technologies installed by professionals. As such, there is effort to find Pb-free alternatives. Although most of the effort has been in PV,^[81,104] an increasing number of groups are investigating Pb-free alternatives to perovskites for emitters.^[105] One approach is to chemically substitute Pb in the ABX₃ structure with Ge, Sn, or Bi. However, these materials have typically exhibited low PLQEs. For example, methylammonium tin iodide has a reported PLQE of 5.3%,^[105] phenethylammonium tin iodide up to 0.24%,^[104] methylammonium germanium-tin iodide up to 2%,^[106] and methylammonium bismuth iodide ≈0.4%.^[107] There are therefore only few examples of room-temperature electroluminescence from these materials and, in the examples that exist, the external quantum efficiency is low.^[105,108] Other approaches to find lead-free alternatives to

the perovskites identify materials that can replicate the crystallographic or electronic structure of established halide perovskites. The former has led to the exploration of double perovskites, which is comprised of two superimposed perovskite lattices based on 1+ and 3+ B-site cations (e.g., Cs₂AgBiBr₆).^[109] The latter has led to the exploration of compounds based on partially oxidized p-block cations, e.g., In⁺, Sb³⁺, and Bi³⁺. These “perovskite-inspired” materials include BiI₃^[110] and BiOI,^[111] which have been found to replicate the electronic structure of lead-halide perovskites.^[104] Although room-temperature photoluminescence has been found in double perovskites and perovskite-inspired materials, the PLQEs are low (<1%) in most currently reported cases.^[104,112]

Recently, Tang and co-workers have achieved orders of magnitude higher PLQEs by investigating A₃B₂X₉ quantum dots (A is a monovalent cation, B is Bi or Sb, and X is a halide). PLQEs of 12% were observed for (CH₃NH₃)₃Bi₂Br₉ (423 nm emission),^[113] 15% for (CH₃NH₃)₃Bi₂Cl₉ (360 nm emission),^[113] 19.4% from Cs₃Bi₂Br₉ (410 nm emission),^[114] 26.4% from Cs₃Bi₂Cl₉ (393 nm emission),^[114] and 46% from Cs₃Sb₂Br₉ (410 nm wavelength).^[115] These materials therefore have potential for blue emitters, where the EQE of PeLEDs are low (below 1% at the time of writing).^[116] However, electroluminescence has yet to be demonstrated from these materials, although Cs₃Bi₂Br₉ quantum dots mixed with YAG have been used as a phosphor over GaN LEDs, resulting in white emission with CIE coordinates of (0.29, 0.30).^[114] The inorganic quantum dots have also been shown to be more stable in water than methylammonium lead iodide. For Cs₃Bi₂Br₉, water exposure has been found to be advantageous, with the PLQE increasing over time; this is similar to the beneficial effects of humidity in MAPbI₃ with short exposure times.^[10,117] The passivation of Cs₃Bi₂Br₉ has been attributed to the formation of a BiOBr layer on the surface.^[114]

Although there is a huge family of lead-free perovskite emitters that can be explored, we have yet to see emitters with comparable luminescence efficiencies to the lead-based materials.

8. Conclusion

Metal halide perovskites are exciting materials for a range of light harvesting and emission applications. Their properties lend them to excellent optoelectronic performance: high intrinsic luminescence yields and tolerance to passivation approaches mean that nonradiative losses can be significantly suppressed, and photon recycling effect opens the door for strong outcoupling in the forward direction in LEDs, as well as high photon and charge-carrier concentrations in solar cells. Although a number of challenges must be overcome before we see their large-scale commercialization as solar absorbers or light emitters in panel lighting or displays, metal-halide perovskites have the potential to significantly disrupt both the power generation and lighting industries.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

light-emitting diodes, luminescence, nonradiative decay, perovskites, solar cells

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- [1] A. Polman, H. A. Atwater, *Nat. Mater.* **2012**, *11*, 174.
- [2] O. D. Miller, E. Yablonovitch, S. R. Kurtz, *IEEE J. Photovoltaics* **2012**, *2*, 303.
- [3] S. D. Stranks, H. J. Snaith, *Nat. Nanotechnol.* **2015**, *10*, 391.
- [4] a) J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, *Science* **2017**, *358*, 739; b) H. J. Snaith, *Nat. Mater.* **2018**, *17*, 372.
- [5] S. D. Stranks, *ACS Energy Lett.* **2017**, *2*, 1515.
- [6] J. M. Ball, A. Petrozza, *Nat. Energy* **2016**, *1*, 16149.
- [7] F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D. D. Jarausch, R. Higler, S. Hüttner, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Atature, R. T. Phillips, R. H. Friend, *J. Phys. Chem. Lett.* **2014**, *5*, 1421.
- [8] M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Cacovich, C. Stavrakas, B. Philippe, J. M. Richter, M. Alsari, E. P. Booker, E. M. Hutter, A. J. Pearson, S. Lilliu, T. J. Savenije, H. Rensmo, G. Divitini, C. Ducati, R. H. Friend, S. D. Stranks, *Nature* **2018**, *555*, 497.
- [9] I. L. Braly, D. W. deQuilettes, L. M. Pazos-Outón, S. Burke, M. E. Ziffer, D. S. Ginger, H. W. Hillhouse, *Nat. Photonics* **2018**, *12*, 355.
- [10] R. Brenes, D. Guo, A. Osherov, N. K. Noel, C. Eames, E. M. Hutter, S. K. Pathak, F. Niroui, R. H. Friend, M. S. Islam, H. J. Snaith, V. Bulović, T. J. Savenije, S. D. Stranks, *Joule* **2017**, *1*, 155.
- [11] L. M. Pazos-Outón, M. Szumilo, R. Lamboll, J. M. Richter, M. Crespo-Quesada, M. Abdi-Jalebi, H. J. Beeson, M. Vručinić, M. Alsari, H. J. Snaith, B. Ehrler, R. H. Friend, F. Deschler, *Science* **2016**, *351*, 1430.
- [12] J. M. Richter, M. Abdi-Jalebi, A. Sadhanala, M. Tabachnyk, J. P. H. Rivett, L. M. Pazos-Outón, K. C. Gödel, M. Price, F. Deschler, R. H. Friend, *Nat. Commun.* **2016**, *7*, 13941.
- [13] W. S. Yang, B. W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, S. I. Seok, *Science* **2017**, *356*, 1376.
- [14] a) M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, *Science* **2012**, *338*, 643; b) H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Grätzel, N. G. Park, *Sci. Rep.* **2012**, *2*, 591; c) A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [15] H. J. Snaith, *J. Phys. Chem. Lett.* **2013**, *4*, 3623.
- [16] S. D. Stranks, P. K. Nayak, W. Zhang, T. Stergiopoulos, H. J. Snaith, *Angew. Chem.* **2015**, *54*, 3240.
- [17] a) J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, *Nano Lett.* **2013**, *13*, 1764; b) G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, H. J. Snaith, *Energy Environ. Sci.* **2014**, *7*, 982; c) W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Science* **2015**, *348*, 1234.
- [18] M. Saliba, T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, *9*, 1989.
- [19] M. Saliba, T. Matsui, K. Domanski, J. Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J. P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Science* **2016**, *354*, 206.
- [20] a) J. Yao, T. Kirchartz, M. S. Vezie, M. A. Faist, W. Gong, Z. He, H. Wu, J. Troughton, T. Watson, D. Bryant, J. Nelson, *Phys. Rev. Appl.* **2015**, *4*, 014020; b) M. A. Steiner, J. F. Geisz, I. García, D. J. Friedman, A. Duda, S. R. Kurtz, *J. Appl. Phys.* **2013**, *113*, 123109.
- [21] Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, *9*, 687.
- [22] a) D. Di, K. P. Musselman, G. Li, A. Sadhanala, Y. Ievskaya, Q. Song, Z.-K. Tan, M. L. Lai, J. L. MacManus-Driscoll, N. C. Greenham, R. H. Friend, *J. Phys. Chem. Lett.* **2015**, *6*, 446; b) G. Li, F. W. R. Rivaola, N. J. L. K. Davis, S. Bai, T. C. Jellicoe, F. de la Peña, S. Hou, C. Ducati, F. Gao, R. H. Friend, N. C. Greenham, Z.-K. Tan, *Adv. Mater.* **2016**, *28*, 3528.
- [23] G. Li, Z. K. Tan, D. Di, M. L. Lai, L. Jiang, J. H. Lim, R. H. Friend, N. C. Greenham, *Nano Lett.* **2015**, *15*, 2640.
- [24] J. Wang, N. Wang, Y. Jin, J. Si, Z.-K. Tan, H. Du, L. Cheng, X. Dai, S. Bai, H. He, Z. Ye, M. L. Lai, R. H. Friend, W. Huang, *Adv. Mater.* **2015**, *27*, 2311.
- [25] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, *Science* **2015**, *350*, 1222.
- [26] Z. Xiao, R. A. Kerner, L. Zhao, N. L. Tran, K. M. Lee, T.-W. Koh, G. D. Scholes, B. P. Rand, *Nat. Photonics* **2017**, *11*, 108.
- [27] M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim, E. H. Sargent, *Nat. Nanotechnol.* **2016**, *11*, 872.
- [28] N. Wang, L. Cheng, R. Ge, S. Zhang, Y. Miao, W. Zou, C. Yi, Y. Sun, Y. Cao, R. Yang, Y. Wei, Q. Guo, Y. Ke, M. Yu, Y. Jin, Y. Liu, Q. Ding, D. Di, L. Yang, G. Xing, H. Tian, C. Jin, F. Gao, R. H. Friend, J. Wang, W. Huang, *Nat. Photonics* **2016**, *10*, 699.
- [29] X. Yang, X. Zhang, J. Deng, Z. Chu, Q. Jiang, J. Meng, P. Wang, L. Zhang, Z. Yin, J. You, *Nat. Commun.* **2018**, *9*, 570.
- [30] a) H. J. Snaith, *Nat. Photonics* **2012**, *6*, 337; b) N. C. Greenham, R. H. Friend, D. D. C. Bradley, *Adv. Mater.* **1994**, *6*, 491; c) S. R. Forrest, D. D. C. Bradley, M. E. Thompson, *Adv. Mater.* **2003**, *15*, 1043.
- [31] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* **2014**, *8*, 506.
- [32] S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum, C. Ballif, *J. Phys. Chem. Lett.* **2014**, *5*, 1035.
- [33] A. Sadhanala, F. Deschler, T. H. Thomas, S. E. Dutton, K. C. Goedel, F. C. Hanusch, M. L. Lai, U. Steiner, T. Bein, P. Docampo, D. Cahen, R. H. Friend, *J. Phys. Chem. Lett.* **2014**, *5*, 2501.
- [34] J. T.-W. Wang, Z. Wang, S. Pathak, W. Zhang, D. W. deQuilettes, F. Wisnivesky-Rocca-Rivarola, J. Huang, P. K. Nayak, J. B. Patel, H. A. Mohd Yusof, Y. Vaynzof, R. Zhu, I. Ramirez, J. Zhang, C. Ducati, C. Grovenor, M. B. Johnston, D. S. Ginger, R. J. Nicholas, H. J. Snaith, *Energy Environ. Sci.* **2016**, *9*, 2892.

- [35] a) S. R. Johnson, T. Tiedje, *J. Appl. Phys.* **1995**, *78*, 5609; b) G. D. Cody, *J. Non-Cryst. Solids* **1992**, *141*, 3.
- [36] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, L. M. Herz, *J. Phys. Chem. Lett.* **2014**, *5*, 1300.
- [37] R. T. Ross, *J. Chem. Phys.* **1967**, *46*, 4590.
- [38] a) M. A. Green, S. P. Bremner, *Nat. Mater.* **2017**, *16*, 23; b) M. A. Green, *Prog. Photovoltaics* **2012**, *20*, 472.
- [39] Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn, P. Meredith, *Nat. Photonics* **2014**, *9*, 106.
- [40] A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, *Nat. Phys.* **2015**, *11*, 582.
- [41] a) M. Saba, M. Cadelano, D. Marongiu, F. Chen, V. Sarritzu, N. Sestu, C. Figus, M. Aresti, R. Piras, A. G. Lehmann, C. Cannas, A. Musinu, F. Quochi, A. Mura, G. Bongiovanni, *Nat. Commun.* **2014**, *5*, 5049; b) L. M. Herz, *Annu. Rev. Phys. Chem.* **2016**, *67*, 65.
- [42] a) E. M. Hutter, G. E. Eperon, S. D. Stranks, T. J. Savenije, *J. Phys. Chem. Lett.* **2015**, *6*, 3082; b) S. D. Stranks, V. M. Burlakov, T. Leijtens, J. M. Ball, A. Goriely, H. J. Snaith, *Phys. Rev. Appl.* **2014**, *2*, 034007.
- [43] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Mater.* **2014**, *26*, 1584.
- [44] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science* **2013**, *342*, 341.
- [45] M. B. Johnston, L. M. Herz, *Acc. Chem. Res.* **2016**, *49*, 146.
- [46] a) R. D. Cunningham, R. W. Brander, N. D. Knee, D. K. Wickenden, *J. Lumin.* **1972**, *5*, 21; b) O. Semyonov, A. Subashiev, Z. Chen, S. Luryi, *J. Appl. Phys.* **2010**, *108*, 013101; c) T. Burgess, D. Saxena, S. Mokkaapati, Z. Li, C. R. Hall, J. A. Davis, Y. Wang, L. M. Smith, L. Fu, P. Caroff, H. H. Tan, C. Jagadish, *Nat. Commun.* **2016**, *7*, 11927.
- [47] D. N. Congreve, M. C. Weidman, M. Seitz, W. Paritmongkol, N. S. Dahod, W. A. Tisdale, *ACS Photonics* **2017**, *4*, 476.
- [48] a) O. Yaffe, Y. Guo, L. Z. Tan, D. A. Egger, T. Hull, C. C. Stoumpos, F. Zheng, T. F. Heinz, L. Kronik, M. G. Kanatzidis, J. S. Owen, A. M. Rappe, M. A. Pimenta, L. E. Brus, *Phys. Rev. Lett.* **2017**, *118*, 136001; b) H. Zhu, K. Miyata, Y. Fu, J. Wang, P. P. Joshi, D. Niesner, K. W. Williams, S. Jin, X. Y. Zhu, *Science* **2016**, *353*, 1409.
- [49] a) E. M. Hutter, M. C. Gelvez-Rueda, A. Osherov, V. Bulovic, F. C. Grozema, S. D. Stranks, T. J. Savenije, *Nat. Mater.* **2017**, *16*, 115; b) P. Azarhoosh, S. McKechnie, J. M. Frost, A. Walsh, M. van Schilfgaarde, *APL Mater.* **2016**, *4*, 091501; c) T. Wang, B. Daiber, J. M. Frost, S. A. Mann, E. C. Garnett, A. Walsh, B. Ehrler, *Energy Environ. Sci.* **2017**, *10*, 509.
- [50] D. Niesner, M. Hauck, S. Shrestha, I. Levchuk, G. J. Matt, A. Osvet, M. Batentschuk, C. J. Brabec, H. B. Weber, T. Fauster, **2017**, arXiv:1703.08740.
- [51] C. L. Davies, M. R. Filip, J. B. Patel, T. W. Crothers, C. Verdi, A. D. Wright, R. L. Milot, F. Giustino, M. B. Johnston, L. M. Herz, *Nat. Commun.* **2018**, *9*, 293.
- [52] V. Sarritzu, N. Sestu, D. Marongiu, X. Chang, Q. Wang, S. Masi, S. Colella, A. Rizzo, A. Gocalinska, E. Pelucchi, L. Mercuri Maria, F. Quochi, M. Saba, A. Mura, G. Bongiovanni, *Adv. Opt. Mater.* **2018**, *6*, 1701254.
- [53] S. D. Stranks, P. Plochocka, *Nat. Mater.* **2018**, *17*, 381.
- [54] J.-S. Kim, P. K. H. Ho, N. C. Greenham, R. H. Friend, *J. Appl. Phys.* **2000**, *88*, 1073.
- [55] a) T. Fujii, Y. Gao, R. Sharma, E. L. Hu, S. P. DenBaars, S. Nakamura, *Appl. Phys. Lett.* **2004**, *84*, 855; b) I. Schnitzer, E. Yablonovitch, C. Caneau, T. J. Gmitter, A. Scherer, *Appl. Phys. Lett.* **1993**, *63*, 2174.
- [56] L. M. Pazos-Outón, T. P. Xiao, E. Yablonovitch, *J. Phys. Chem. Lett.* **2018**, *9*, 1703.
- [57] a) J. M. Ball, S. D. Stranks, M. T. Hörantner, S. Hüttner, W. Zhang, E. J. W. Crossland, I. Ramirez, M. Riede, M. B. Johnston, R. H. Friend, H. J. Snaith, *Energy Environ. Sci.* **2015**, *8*, 602; b) M. Anaya, G. Lozano, M. E. Calvo, W. Zhang, M. B. Johnston, H. J. Snaith, H. Míguez, *J. Phys. Chem. Lett.* **2015**, *6*, 48.
- [58] a) X. Wu, L. Z. Tan, X. Shen, T. Hu, K. Miyata, M. T. Trinh, R. Li, R. Coffee, S. Liu, D. A. Egger, I. Makasyuk, Q. Zheng, A. Fry, J. S. Robinson, M. D. Smith, B. Guzelturk, H. I. Karunadasa, X. Wang, X. Zhu, L. Kronik, A. M. Rappe, A. M. Lindenberg, *Sci. Adv.* **2017**, *3*, e1602388; b) G. Y. Kim, A. Senocrate, T.-Y. Yang, G. Gregori, M. Grätzel, J. Maier, *Nat. Mater.* **2018**, *17*, 445; c) Y. Zhou, L. You, S. Wang, Z. Ku, H. Fan, D. Schmidt, A. Rusydi, L. Chang, L. Wang, P. Ren, L. Chen, G. Yuan, L. Chen, J. Wang, *Nat. Commun.* **2016**, *7*, 11193; d) H. Tsai, R. Asadpour, J.-C. Blancon, C. C. Stoumpos, O. Durand, J. W. Strzalka, B. Chen, R. Verduzco, P. M. Ajayan, S. Tretiak, J. Even, M. A. Alam, M. G. Kanatzidis, W. Nie, A. D. Mohite, *Science* **2018**, *360*, 67.
- [59] a) R. K. Ahrenkiel, D. J. Dunlavy, B. Keyes, S. M. Vernon, T. M. Dixon, S. P. Tobin, K. L. Miller, R. E. Hayes, *Appl. Phys. Lett.* **1989**, *55*, 1088; b) A. Martí, J. L. Balenzategui, R. F. Reyna, *J. Appl. Phys.* **1997**, *82*, 4067.
- [60] V. D'Innocenzo, G. Grancini, M. J. Alcocer, A. R. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith, A. Petrozza, *Nat. Commun.* **2014**, *5*, 3586.
- [61] S. D. Stranks, A. Petrozza, *Nat. Photonics* **2016**, *10*, 562.
- [62] D. W. deQuilettes, S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith, D. S. Ginger, *Science* **2015**, *348*, 683.
- [63] S. Draguta, S. Thakur, Y. V. Morozov, Y. Wang, J. S. Manser, P. V. Kamat, M. Kuno, *J. Phys. Chem. Lett.* **2016**, *7*, 715.
- [64] a) W.-J. Yin, T. Shi, Y. Yan, *Appl. Phys. Lett.* **2014**, *104*, 063903; b) M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, *Science* **2017**, *358*, 745; c) A. Walsh, A. Zunger, *Nat. Mater.* **2017**, *16*, 964.
- [65] T. Kirchartz, T. Markvart, U. Rau, D. A. Egger, *J. Phys. Chem. Lett.* **2018**, *9*, 939.
- [66] D. W. deQuilettes, S. Koch, S. Burke, R. K. Paranj, A. J. Shropshire, M. E. Ziffer, D. S. Ginger, *ACS Energy Lett.* **2016**, *1*, 438.
- [67] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, H. J. Snaith, *ACS Nano* **2014**, *8*, 9815.
- [68] a) H.-H. Fang, S. Adjokatse, H. Wei, J. Yang, G. R. Blake, J. Huang, J. Even, M. A. Loi, *Sci. Adv.* **2016**, *2*, e1600534; b) D. W. deQuilettes, W. Zhang, V. M. Burlakov, D. J. Graham, T. Leijtens, A. Osherov, V. Bulovic, H. J. Snaith, D. S. Ginger, S. D. Stranks, *Nat. Commun.* **2016**, *7*, 11683; c) Y. Tian, M. Peter, E. Unger, M. Abdellah, K. Zheng, T. Pullerits, A. Yartsev, V. Sundstrom, I. G. Scheblykin, *Phys. Chem. Chem. Phys.* **2015**, *17*, 24978; d) J. F. Galisteo-López, M. Anaya, M. E. Calvo, H. Míguez, *J. Phys. Chem. Lett.* **2015**, *6*, 2200.
- [69] R. Brenes, C. Eames, V. Bulovic, M. S. Islam, S. D. Stranks, *Adv. Mater.* **2018**, *30*, e1706208.
- [70] N. Aristidou, C. Eames, I. Sanchez-Molina, X. Bu, J. Kosco, M. S. Islam, S. A. Haque, *Nat. Commun.* **2017**, *8*, 15218.
- [71] a) M. C. Weidman, M. Seitz, S. D. Stranks, W. A. Tisdale, *ACS Nano* **2016**, *10*, 7830; b) X. Gong, O. Voznyy, A. Jain, W. Liu, R. Sabatini, Z. Piontkowski, G. Walters, G. Bappi, S. Nokhrin, O. Bushuyev, M. Yuan, R. Comin, D. McCamant, S. O. Kelley, E. H. Sargent, *Nat. Mater.* **2018**, *17*, 550.
- [72] K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov, H. J. Bolink, *Sci. Rep.* **2014**, *4*, 6071.
- [73] O. A. Jaramillo-Quintero, R. S. Sanchez, M. Rincon, I. Mora-Sero, *J. Phys. Chem. Lett.* **2015**, *6*, 1883.
- [74] M. Wolff Christian, F. Zu, A. Paulke, P. Toro Lorena, N. Koch, D. Neher, *Adv. Mater.* **2017**, *29*, 1700159.
- [75] L. Zhang, X. Yang, Q. Jiang, P. Wang, Z. Yin, X. Zhang, H. Tan, Y. Yang, M. Wei, B. R. Sutherland, E. H. Sargent, J. You, *Nat. Commun.* **2017**, *8*, 15640.
- [76] S. Lee, J. H. Park, B. R. Lee, E. D. Jung, J. C. Yu, D. Di Nuzzo, R. H. Friend, M. H. Song, *J. Phys. Chem. Lett.* **2017**, *8*, 1784.

- [77] a) R. L. Z. Hoyer, M. R. Chua, K. P. Musselman, G. Li, M.-L. Lai, Z.-K. Tan, N. C. Greenham, J. L. MacManus-Driscoll, R. H. Friend, D. Credgington, *Adv. Mater.* **2015**, 27, 1414; b) R. L. Z. Hoyer, D. Muñoz-Rojas, K. P. Musselman, Y. Vaynzof, J. L. MacManus-Driscoll, *ACS Appl. Mater. Interfaces* **2015**, 7, 10684.
- [78] a) Y. H. Kim, H. Cho, J. H. Heo, T. S. Kim, N. Myoung, C. L. Lee, S. H. Im, T. W. Lee, *Adv. Mater.* **2015**, 27, 1248; b) D. B. Kim, J. C. Yu, Y. S. Nam, D. W. Kim, E. D. Jung, S. Y. Lee, S. Lee, J. H. Park, A.-Y. Lee, B. R. Lee, D. Di Nuzzo, R. H. Friend, M. H. Song, *J. Mater. Chem. C* **2016**, 4, 8161.
- [79] A. Sadhanala, S. Ahmad, B. Zhao, N. Giesbrecht, P. M. Pearce, F. Deschler, R. L. Z. Hoyer, K. C. Gödel, T. Bein, P. Docampo, S. E. Dutton, M. F. L. De Volder, R. H. Friend, *Nano Lett.* **2015**, 15, 6095.
- [80] a) Y.-H. Kim, H. Cho, T.-W. Lee, *Proc. Natl. Acad. Sci. USA* **2016**, 113, 11694; b) A. Veldhuis Sjoerd, P. Boix Pablo, N. Yantara, M. Li, C. Sum Tze, N. Mathews, G. Mhaisalkar Subodh, *Adv. Mater.* **2016**, 28, 6804.
- [81] R. L. Z. Hoyer, P. Schulz, L. T. Schelhas, A. M. Holder, K. H. Stone, J. D. Perkins, D. Vigil-Fowler, S. Siol, D. O. Scanlon, A. Zakutayev, A. Walsh, I. C. Smith, B. C. Melot, R. C. Kurchin, Y. Wang, J. Shi, F. C. Marques, J. J. Berry, W. Tumas, S. Lany, V. Stevanović, M. F. Toney, T. Buonassisi, *Chem. Mater.* **2017**, 29, 1964.
- [82] R. L. Z. Hoyer, K. P. Musselman, M. R. Chua, A. Sadhanala, R. D. Raninga, J. L. MacManus-Driscoll, R. H. Friend, D. Credgington, *J. Mater. Chem. C* **2015**, 3, 9327.
- [83] T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, W. J. Feast, *Appl. Phys. Lett.* **1999**, 75, 1679.
- [84] E. Amerling, S. Baniya, E. Lafalce, C. Zhang, Z. V. Vardeny, L. Whittaker-Brooks, *J. Phys. Chem. Lett.* **2017**, 8, 4557.
- [85] M. E. Ziffer, J. C. Mohammed, D. S. Ginger, *ACS Photonics* **2016**, 3, 1060.
- [86] I. H. Campbell, T. W. Hagler, D. L. Smith, J. P. Ferraris, *Phys. Rev. Lett.* **1996**, 76, 1900.
- [87] G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Gratzel, S. Mhaisalkar, T. C. Sum, *Science* **2013**, 342, 344.
- [88] H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, C. M. M. Soe, J. Yoo, J. Crochet, S. Tretiak, J. Even, A. Sadhanala, G. Azzellino, R. Brenes, P. M. Ajayan, V. Bulović, S. D. Stranks, R. H. Friend, M. G. Kanatzidis, A. D. Mohite, *Adv. Mater.* **2018**, 30, 170217.
- [89] Y. Yuan, J. Huang, *Acc. Chem. Res.* **2016**, 49, 286.
- [90] W. Zou, R. Li, S. Zhang, Y. Liu, N. Wang, Y. Cao, Y. Miao, M. Xu, Q. Guo, D. Di, L. Zhang, C. Yi, F. Gao, R. H. Friend, J. Wang, W. Huang, *Nat. Commun.* **2018**, 9, 608.
- [91] S. Möller, S. R. Forrest, *J. Appl. Phys.* **2002**, 91, 3324.
- [92] a) A. Dodabalapur, L. J. Rothberg, T. M. Miller, E. W. Kwock, *Appl. Phys. Lett.* **1994**, 64, 2486; b) A. Dodabalapur, L. J. Rothberg, R. H. Jordan, T. M. Miller, R. E. Slusher, J. M. Phillips, *J. Appl. Phys.* **1996**, 80, 6954.
- [93] M. Kitamura, S. Iwamoto, Y. Arakawa, *Appl. Phys. Lett.* **2005**, 87, 151119.
- [94] a) Z. Ning, X. Gong, R. Comin, G. Walters, F. Fan, O. Voznyy, E. Yassitepe, A. Buin, S. Hoogland, E. H. Sargent, *Nature* **2015**, 523, 324; b) Y.-H. Kim, C. Wolf, Y.-T. Kim, H. Cho, W. Kwon, S. Do, A. Sadhanala, C. G. Park, S.-W. Rhee, S. H. Im, R. H. Friend, T.-W. Lee, *ACS Nano* **2017**, 11, 6586.
- [95] Q. Lin, Z. Wang, J. Snaith Henry, B. Johnston Michael, M. Herz Laura, *Adv. Sci.* **2018**, 5, 1700792.
- [96] a) D. Di, A. S. Romanov, L. Yang, J. M. Richter, J. P. H. Rivett, S. Jones, T. H. Thomas, M. Abdi Jalebi, R. H. Friend, M. Linnolahti, M. Bochmann, D. Credgington, *Science* **2017**, 356, 159; b) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, 492, 234.
- [97] B. R. Sutherland, E. H. Sargent, *Nat. Photonics* **2016**, 10, 295.
- [98] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, D. Cahen, *Nat. Rev. Mater.* **2016**, 1, 15007.
- [99] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, 395, 151.
- [100] D. Di, L. Yang, M. Richter Johannes, L. Meraldi, M. Altamimi Rashid, Y. Alyamani Ahmed, D. Credgington, P. Musselman Kevin, L. MacManus-Driscoll Judith, H. Friend Richard, *Adv. Mater.* **2017**, 29, 1605987.
- [101] a) X. Dai, Y. Deng, X. Peng, Y. Jin, *Adv. Mater.* **2017**, 29, 1607022; b) S. Abe, J. J. Joos, L. I. D. J. Martin, Z. Hens, P. F. Smet, *Light: Sci. Appl.* **2017**, 6, e16271.
- [102] *Off. J. Eur. Union* **2017**, L281/29.
- [103] A. Abate, *Joule* **2017**, 1, 659.
- [104] R. E. Brandt, J. R. Poindexter, P. Gorai, R. C. Kurchin, R. L. Z. Hoyer, L. Nienhaus, M. W. B. Wilson, J. A. Polizzotti, R. Sereika, R. Žaltauskas, L. C. Lee, J. L. MacManus-Driscoll, M. Bawendi, V. Stevanović, T. Buonassisi, *Chem. Mater.* **2017**, 29, 4667.
- [105] M. L. Lai, T. Y. S. Tay, A. Sadhanala, S. E. Dutton, G. Li, R. H. Friend, Z.-K. Tan, *J. Phys. Chem. Lett.* **2016**, 7, 2653.
- [106] S. Nagane, D. Ghosh, R. L. Z. Hoyer, B. Zhao, S. Ahmad, A. B. Walker, M. S. Islam, S. Ogale, A. Sadhanala, *J. Phys. Chem. C* **2018**, 122, 5940.
- [107] R. L. Z. Hoyer, R. E. Brandt, A. Osherov, V. Stevanović, S. D. Stranks, M. W. Wilson, H. Kim, A. J. Akey, J. D. Perkins, R. C. Kurchin, J. R. Poindexter, E. N. Wang, M. G. Bawendi, V. Bulovic, T. Buonassisi, *Chem. – Eur. J.* **2016**, 22, 2605.
- [108] L. Lanzetta, J. M. Marin-Beloqui, I. Sanchez-Molina, D. Ding, S. A. Haque, *ACS Energy Lett.* **2017**, 2, 1662.
- [109] A. H. Slavney, T. Hu, A. M. Lindenberg, H. I. Karunadasa, *J. Am. Chem. Soc.* **2016**, 138, 2138.
- [110] R. E. Brandt, R. C. Kurchin, R. L. Z. Hoyer, J. R. Poindexter, M. W. B. Wilson, S. Sulekar, F. Lenahan, P. X. T. Yen, V. Stevanović, J. C. Nino, M. G. Bawendi, T. Buonassisi, *J. Phys. Chem. Lett.* **2015**, 6, 4297.
- [111] R. L. Z. Hoyer, C. Lee Lana, C. Kurchin Rachel, N. Huq Tahmida, H. L. Zhang Kelvin, M. Sponseller, L. Nienhaus, E. Brandt Riley, J. Jean, A. Polizzotti James, A. Kursumović, G. Bawendi Mounqi, V. Bulović, V. Stevanović, T. Buonassisi, J. L. MacManus-Driscoll Judith, *Adv. Mater.* **2017**, 29, 1702176.
- [112] R. L. Z. Hoyer, L. Eyre, F. Wei, F. Brivio, A. Sadhanala, S. Sun, W. Li, K. Zhang, J. L. MacManus-Driscoll, P. D. Bristowe, R. H. Friend, A. Cheetham, F. Deschler, *Adv. Mater. Interfaces* **2018**, 5, 1800464.
- [113] M. Leng, Z. Chen, Y. Yang, Z. Li, K. Zeng, K. Li, G. Niu, Y. He, Q. Zhou, J. Tang, *Angew. Chem., Int. Ed.* **2016**, 55, 15012.
- [114] M. Leng, Y. Yang, K. Zeng, Z. Chen, Z. Tan, S. Li, J. Li, B. Xu, D. Li, P. Hautzinger Matthew, Y. Fu, T. Zhai, L. Xu, G. Niu, S. Jin, J. Tang, *Adv. Funct. Mater.* **2017**, 28, 1704446.
- [115] J. Zhang, Y. Yang, H. Deng, U. Farooq, X. Yang, J. Khan, J. Tang, H. Song, *ACS Nano* **2017**, 11, 9294.
- [116] K. Gangishetty Mahesh, S. Hou, Q. Quan, N. Congreve Daniel, *Adv. Mater.* **2018**, 30, 1706226.
- [117] G. E. Eperon, S. N. Habisreutinger, T. Leijtens, B. J. Bruijnaers, J. J. van Franeker, D. W. deQuilettes, S. Pathak, R. J. Sutton, G. Grancini, D. S. Ginger, R. A. Janssen, A. Petrozza, H. J. Snaith, *ACS Nano* **2015**, 9, 9380.