Photon Reabsorption in Mixed CsPbCl₃:CsPbI₃ Perovskite Nanocrystal Films for Light-Emitting Diodes

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Supporting Information

ABSTRACT: Cesium lead halide nanocrystals, CsPbX₃ (X = Cl, Br, I), exhibit photoluminescence quantum efficiencies approaching 100% without the core–shell structures usually used in conventional semiconductor nanocrystals. These high photoluminescence efficiencies make these crystals ideal candidates for light-emitting diodes (LEDs). However, because of the large surface area to volume ratio, halogen exchange between perovskite nanocrystals of different compositions occurs rapidly, which is one of the limiting factors for white-light applications requiring a mixture of different crystal compositions to achieve a broad emission spectrum. Here, we use mixtures of chloride and iodide CsPbX₃ (X = Cl, I) perovskite nanocrystals where anion exchange is significantly reduced. We investigate samples containing mixtures of perovskite nanocrystals with different compositions and study the resulting optical and electrical interactions. We report excitation transfer from CsPbCl₃ to CsPbI₃ in solution and within a poly(methyl methacrylate) matrix via photon reabsorption, which also occurs in electrically excited crystals in bulk heterojunction LEDs.

INTRODUCTION

Low-cost solution-processable metal halide perovskite semiconductors have seen encouraging development as inexpensive absorber layers in solar cells, and show high mobility, bright emission, tunable band gap, and photon recycling. Power conversion efficiencies for perovskite solar cells have exceeded 20%. While the majority of research has focused on thin-film and bulk materials, perovskite nanocrystals have recently been synthesized. These include hybrid organic–inorganic MAPbX₃ (MA = methylammonium, X = Cl, Br, I) nanocrystals and nanostructures as well as all-inorganic cesium lead halide CsPbX₃ (X = Cl, Br, I) and cesium tin halide CsSnX₃ (X = Cl, Br, I) nanocrystals and nanostructures. The move to colloidal semiconductor quantum dots not only improves solution processability of these materials but also allows band gap tunability due to three-dimensional (3D) confinement effects and creates a material that is readily miscible with other optoelectronic materials, for example, polymers, fullerenes, and other nanomaterials. Hybrid organic–inorganic lead halide perovskite nanostructures have been used in detectors for the visible, ultraviolet, and X-ray regions of the electromagnetic spectrum as gain media for optically pumped lasers, and as emission layers for light-emitting diodes (LEDs).

It has been reported that in perovskites ABX₃ (A = MA, Cs; B = Pb, Sn; X = Cl, Br, I) the ratios of the different halide components have a strong influence on the electronic properties of the material. The ability of the halide ions to migrate within bulk perovskite has been reported both for MAPbX₃ and for CsPbX₃, which has specifically been identified as a halide-ion conductor. The high ion mobility within perovskite crystals has been recognized as a possible source for the hysteresis in the current–voltage curves seen in photovoltaic devices. In CsPbX₃ nanocrystals, which have a high surface area to volume ratio, halide exchange quickly incorporates new sources of excess halides, resulting in a shift of the optical band gap. This is also the case when crystals with different halide compositions are mixed, resulting in the formation of crystals with an averaged total halide composition. Halide exchange has been shown to be possible in both MAPbX₃ and CsPbX₃ when moving between periodically adjacent halides, for example, from CsPbCl₃ to CsPbBr₃ and CsPbBr₃ to CsPbI₃ and vice versa.

Although recently there has been an increase in the application of CsPbX₃ nanocrystals, the inability of CsPbX₃ nanocrystals with different compositions to coexist as discrete semiconductors in one sample without rapid halide exchange significantly limits their use in applications where multiple band gaps are required, such as white-light LEDs and...
exciton concentration systems. Recently, Palazon et al.\textsuperscript{41} showed that cross-linking the surface ligands in neat nanocrystal films improves stability, prevents film liftoff, and limits halogen exchange. It has also been shown that wrapping clusters of CsPbX\textsubscript{3} nanocrystals in polyhedral oligomeric silsesquioxane cages can prevent halogen exchange.\textsuperscript{42} However, neither of these methods allows the formation of films where the nanocrystals are mixed on the submicrometer scale.

Energy transfer from high band gap to low band gap nanocrystals has been demonstrated between CsPbBr\textsubscript{3} particles\textsuperscript{43} and CsPbI\textsubscript{3} particles.\textsuperscript{44} Interactions between CsPbCl\textsubscript{3} and CsPbI\textsubscript{3} nanocrystals have been previously reported to lead to dissolution of the nanocrystals.\textsuperscript{33} We find that when the crystals are synthesized and kept in an oxygen- and water-free environment, this is not the case, consistent with a recent report by Dastidar et al.\textsuperscript{44} We report significantly reduced halide exchange between chloride and iodide in CsPbX\textsubscript{3} (X = Cl, I) perovskite nanocrystals because of the unfavorable crystal lattice tolerance factor for iodide–chloride exchange in this system. This allows us to investigate films and solutions containing nanocrystals of differing compositions, and to study the resulting optical and electronic interactions. Efficient excitation transfer from CsPbCl\textsubscript{3} to CsPbI\textsubscript{3} is found to proceed by a radiative process. Excitation transfer also occurs in electrically pumped crystals forming the active layer of a bulk heterojunction LED. CsPbCl\textsubscript{3} emission can efficiently be reabsorbed by the CsPbI\textsubscript{3} nanocrystals and re-emitted in the red region.

## METHODS

All chemicals were purchased from Sigma-Aldrich (St. Louis) and were used as received.

**Synthesis of CsPbX\textsubscript{3} (X = Cl, I) Nanocrystals.** Perovskite nanocrystals were synthesized using previously reported procedures.\textsuperscript{39} Cs\textsubscript{2}CO\textsubscript{3} (0.814g, 99.9%) was loaded into 100 mL three-neck flask along with octadecene (ODE, 30 mL, 90%) and oleic acid (2.5 mL, 90%), and the mixture was dried for 2 h at 120 °C under N\textsubscript{2}. The solution temperature was then lowered to 100 °C. ODE (75 mL), oleylamine (7.5 mL, OLA, 90%), and dried OA (7.5 mL) and PbX\textsubscript{2} (2.82 mmol) such as PbI\textsubscript{2} (1.26 g, 99.99%) and PbCl\textsubscript{2} (0.675g, 99%) were added to solubilize PbCl\textsubscript{2}. The nanocrystals were transferred to an OA, 90%), and the mixture was dried for 2 h at 120 °C. Synthesis of CsPbX\textsubscript{3} (X = Cl, I) solutions at 2000 rpm for 15 s, or for 10 mg mL\textsuperscript{−1} poly(9-vinylcarbazole) (PVK) in toluene was spin-coated at 2000 rpm for 60 s. Photoluminescence was measured on an Edinburgh Instruments FLS980 fluorimeter. Solution samples were measured in a 1 cm × 0.3 cm cuvette excited in the 1 cm direction and imaged in the 0.3 cm direction. Film samples were excited by front face illumination at 45° to the surface; detection was at 90° to excitation and also at 45° to the surface.

**Monte Carlo Simulations.** A Monte Carlo simulation of the expected photoluminescence (PL) was constructed, using only the measured emission and absorption spectra of the constituent species. Photons are generated, traveling in random directions from the middle axis. The model is two-dimensional, allowing light to leave the system in either the small or large axis, with dimensions of 0.3 or 3 cm. Photon travel lengths are randomly generated, consistent with the concentration- and wavelength-dependent absorption lengths arising from the two species in the mix. The travel distance is then the shorter of these two distances. If this length takes the photon outside the container, it is counted toward the final spectrum if it leaves via the small axis and ignored if it leaves via the large axis. Otherwise, it has a chance equal to the pure substance photoluminescence quantum efficiency (PLQE) of being re-emitted by the species that absorbed it, in a new random direction and according to that species’ emission spectrum. All values required can be measured from the single-species solutions, and so the model contains no fitted parameters.

**Time-Correlated Single-Photon Counting (TCSPC) Measurements.** The samples were prepared on quartz glass by spin coating from a 10 mg mL\textsuperscript{−1} perovskite nanocrystal dispersion in 10 mg mL\textsuperscript{−1} PVK in toluene at 2000 rpm for 60 s. The nanocrystal films were encapsulated by affixing a glass coverslip on the nanocrystal layer using carbon tape as a spacer unit and epoxy glue as a sealant. The samples were excited by front face illumination at 45° to the surface; detection was at 90° to excitation and also at 45° to the surface.

**Transmission Electron Microscopy (TEM).** TEM samples were prepared by drop-casting an ca. 40 mg mL\textsuperscript{−1} perovskite crystals solution in octane on a TEM Grid (200 mesh Cu, Agar Scientific) in a argon-filled glove box. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and electron energy loss spectroscopy (EELS) analysis was also conducted on a FEI Tecnai Osiris STEM/STEM 80-200 microscope, operating at 80 kV, using a liquid nitrogen holder, and equipped with a Gatan Enfinium ER 977 spectrometer with dual EELS. The convergence and collection angles used were 8.5 and 34 mrad, respectively. The EELS spectral images were analyzed using principal component analysis and the elemental maps with the absolute quantification were obtained through the use of the integration method proposed by Egerton.\textsuperscript{45} The EELS data analysis and elemental quantification were performed using the open source software package HyperSpy toolbox.

**X-ray Diffraction (XRD).** Perovskite nanocrystal films were prepared by drop-coating a 10 mg mL\textsuperscript{−1} nanocrystals solution in hexane on silicon wafers. XRD experiments were carried out on a Bruker X-ray diffractometer using a Cu Kα radiation source (\(\lambda = 1.5418\) Å). The measurements were taken from 2θ of 10° to 70° with a step size of 0.0102° in 2θ.

**Film Thickness.** Film thicknesses were measured using a DEKTAK profilometer and a Digital Instruments/Veco Dimension 3100 atomic force microscope.

**PLQE Measurements.** Nanocrystal films were placed in an integrating sphere and were photoexcited using a 405 nm continuous-wave laser. The laser and the emission signals were measured and quantified using a calibrated Andor iDus DU490A InGaAs detector for the determination of PL quantum efficiency. PLQE was calculated as per de Mello et al.\textsuperscript{46}
were deposited through a shadow mask at $3 \times 10^{-6}$ mbar or better. The LEDs were encapsulated by affixing a glass slide on top of the contacts using transparent ultraviolet (UV) epoxy glue.

**LED Characterization.** Current versus voltage characteristics were measured using a Keithley 2400 source measure unit. Photon flux was measured simultaneously using a calibrated silicon photodiode centered over the light-emitting pixel. Luminance in cd m$^{-2}$ was calculated based on the emission spectrum of the LED, weighted against the standard luminosity function and on the known spectral response of the silicon photodiode. External quantum efficiency was calculated assuming a Lambertian emission profile. Electroluminescence spectra were measured using a Labsphere CDS-610 spectrometer.

### RESULTS AND DISCUSSION

CsPbX$_3$ ($X = \text{Cl, I}$) nanocrystals were prepared as previously reported by Protesescu et al. $^{19}$ (details in the *Methods* section). All processing and characterization were performed in an inert atmosphere (oxygen and water <5 ppm). Under these conditions we find that CsPbCl$_3$ and CsPbI$_3$ nanocrystals coexist in solution without undergoing dissolution or significant halogen exchange. To investigate the optical properties of this system, we prepared solutions of CsPbCl$_3$ and CsPbI$_3$ at an overall crystal concentration of $\approx 1$ mg mL$^{-1}$ (Figure 1a). The respective absorbance spectra are shown in Figure 1a. We find absorbance onsets of 425 and 690 nm for the CsPbCl$_3$ and CsPbI$_3$ samples, respectively. The CsPbCl$_3$ nanocrystals show a sharp peak close to the absorption onset, which likely arises from excitonic effects. Mixed solutions show a combination of the characteristic features of the pure nanocrystal solutions without any spectral shifting. By fitting the absorbance spectrum of the mixed solution with a sum of the pure sample spectra, we calculate the ratio of the different crystals in a nominally 1:1 mixed solution sample to be 1:0.957 (CsPbCl$_3$:CsPbI$_3$) (Figure 1 of the Supporting Information).

To investigate the structural and physical properties of the mixed system by powder XRD and TEM, neat films of the crystals were drop-cast from a 10 mg mL$^{-1}$ solution respectively onto silicon and onto carbon-coated copper substrates. The XRD pattern (Figure 1b) shows peaks at $16^\circ$ and $32.5^\circ$ corresponding to those found in pure CsPbCl$_3$ crystals reported by Protesescu et al. $^{19}$ and similarly at $14^\circ$ and $28^\circ$ in the pure CsPbI$_3$ crystals. The XRD pattern of the CsPbCl$_3$:CsPbI$_3$ (1:1) sample is a superposition of the CsPbCl$_3$ and CsPbI$_3$ nanocrystal XRD patterns. The presence of both CsPbCl$_3$ and CsPbI$_3$ peaks in the blends, without any shifts or additional peaks, indicates that these crystal structures exist in parallel in our nanocrystal blend films. HAADF TEM imaging (Figure 1c) shows two distinct types of nanocrystals with slightly different contrasts and sizes, suggesting two different nanocrystal populations. EELS and scanning transmission electron microscopy (STEM) was then used to further assign these crystal populations and obtain an absolute quantification of each element. The individual elemental maps with number of atoms per nm$^2$, shown in Figure 1c, indicate that the iodide is localized on the larger crystals while the chloride is localized on the smaller crystals. The amount of I and Cl in the nanocrystals maintains a 3:1 stoichiometric ratio with Cs. The EELS spectra measured at the two locations in Figure 1c show two distinct traces for different nanocrystal populations and are shown in Figure 1d. The blue trace, corresponding to EELS measurements at the blue cross, is assigned to a CsPbCl$_3$ nanocrystal with edges seen for Cs, C, Cl, and O, and the red trace, corresponding to EELS measurements at the red cross, is assigned to a CsPbI$_3$ nanocrystal with edges seen for Cs, C, I, and O. The sizes of the CsPbCl$_3$ and CsPbI$_3$ nanocrystals were measured at $7.0 \pm 2.8$ and $12.0 \pm 3.9$ nm, respectively. These data confirm that the CsPbCl$_3$ and CsPbI$_3$ nanocrystals are intimately mixed but remain discrete entities with insignificant halide mixing between them. The data in Figure 1 support our conclusion that CsPbCl$_3$ and CsPbI$_3$ do not undergo significant

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**Figure 1.** (a) Absorption spectra (left) of pure CsPbCl$_3$, CsPbI$_3$, and a 1:1 nanocrystal blend and emission spectra (right) of pure CsPbCl$_3$ and CsPbI$_3$ in hexane (concentration $\approx 1$ mg mL$^{-1}$). (b) Powder XRD patterns of CsPbCl$_3$, CsPbI$_3$, and 1:1 nanocrystal blend solid films with distinctive peak highlighted. (c) HAADF TEM images and EELS TEM maps for Cs, I, and Cl. Scale bar = 20 nm. (d) EELS TEM spectrum for CsPbCl$_3$:CsPbI$_3$ (1:1) samples taken at the positions of the red and blue crosses in (c). Lines indicate atomic absorption edges.
halogen exchange with each other. The lack of halogen exchange in these systems is assigned to the different tolerance factors of the different crystal lattices acting to inhibit halogen exchange.47

The ability of these crystals to exist as discrete entities gives us the unique opportunity to study these crystals and their photophysical interactions with each other. CsPbCl3 nanocrystals emit in the near UV at 425 nm, whereas CsPbI3 nanocrystals emit in the red at 695 nm (Figure 1a). When excited at 365 nm, nanocrystals dispersed in a poly(methyl methacrylate) (PMMA) matrix at a total nanocrystal:polymer ratio of 1:1 by weight (film thickness ≈20 nm) (Figure 2a) and neat mixed nanocrystal films spun from toluene (Figure 2b) clearly show emission from both types of nanocrystals. Spectral tuning of the separate crystals was also achievable by incorporating a small (weight fraction ≤10%) amount of CsPbBr3 nanocrystals in a solution of CsPbCl3 and CsPbI3 nanocrystals. As there is not enough CsPbBr3 to represent a majority, the CsPbBr3 is incorporated into the CsPbCl3 and CsPbI3 crystals, resulting in a CsPbCl3(1−x)Brx and CsPbI3(1−x)Brx blend (Figure 2c).

When the crystals were excited directly at 550 nm, the overall PLQE yield of the CsPbI3 crystals decreased with increasing CsPbCl3 ratios (Figure 2 of the Supporting Information). Despite there being no change in XRD (Figure 3 of the Supporting Information) or the emission spectrum, TEM images show a small amount of chloride ions into the CsPbI3 crystals (Figure 1c; Figure 4 of the Supporting Information). We attribute the decrease in PLQE to small amounts of chloride migration which increases the amount of nonradiative decay within the crystals. This is consistent with TCSPC measurements (Figure 5 of the Supporting Information), which show the CsPbI3 fluorescence decay lifetimes are shortened for ratios greater that 1:1. We are still able to achieve high PLQEs in the CsPbI3 nanocrystals at a 1:1 ratio.

The above spectra (Figure 2a,b) showed emission from both CsPbCl3 and CsPbI3 nanocrystals; however, when CsPbCl3 and CsPbI3 nanocrystals are mixed in a 1:1 ratio at higher solution concentrations and in thicker polymer matrixes, the emission was found to be predominantly at 695 nm under 405 nm excitation. Solutions of CsPbCl3 and CsPbCl3 nanocrystals showed emission solely from the CsPbCl3 crystals up until a 20-fold excess of CsPbCl3 (Figure 6 of the Supporting Information). Emission solely from the low-energy particles was also seen for nanocrystals dispersed in a PMMA matrix at a total nanocrystal:polymer ratio of 1:1 by weight and film thickness ≈75 nm (Figure 3a). These results indicate that there is efficient energy transfer to the low-energy nanocrystals.

Figure 2. (a) Solid-state absorbance and emission spectra of CsPbCl3:CsPbI3 (1:1) in PMMA, film thickness ≈20 nm (10 mg mL−1 nanocrystals and 10 mg mL−1 PMMA in toluene, spun at 6000 rpm). (b) Solid state absorbance and emission in neat mixed crystal films (10 mg mL−1 in toluene, spun at 2000 rpm). (c) Absorbance and emission of ≈0.1 mg mL−1 nanocrystals in toluene) with different CsPbCl3:CsPbBr3:CsPbI3 ratios.

Figure 3. (a) Luminescence of CsPbCl3, CsPbI3, and CsPbCl3:ClPbI3 blends in PMMA matrix at a total nanocrystal:polymer ratio of 1:1 by weight and film thickness ≈75 nm. (b) Transient luminescence decays excited at 405 nm with measurements at 450 or 670 nm.
The interaction responsible for this energy transfer in solid films was investigated through transient spectroscopy techniques. For mixed samples with a 1:1 ratio of CsPbCl₃:CsPbI₃ by weight, the CsPbI₃ nanocrystals show an increased lifetime when excited at 405 nm compared to pure CsPbI₃ samples (Figure 3b). Consistent with steady state measurements, there was no emission from the CsPbCl₃ nanocrystals in the mixed samples. An extended luminescence lifetime in the lower-energy particle is consistent with excitation transfer. One possible mechanism for this energy transfer is Förster resonance energy transfer (FRET). We calculate the Förster radius $R_0$, the distance at which 50% of all excitations lead to energy transfer from the donor to the acceptor, using measured absorption, emission, and PLQE data to be 6.8 ± 0.3 nm. This value is comparable to the size of the nanocrystals so the point dipole approximation stipulated in FRET calculations is not entirely appropriate. It is also worth noting that the large aliphatic ligands that offer colloidal stability are still attached to these crystals. This combined with the apparent slight phase separation of the two crystals in neat films (Figure 1c; Figure 4 of the Supporting Information) and the fact that the crystals are supported in a polymer matrix means that the distance between a CsPbCl₃ and CsPbI₃ particle is generally greater than 6.8 nm. We cannot completely rule out FRET playing a role in energy transfer, but crucially the fact that energy transfer is more efficient reabsorption of photons occurring from the CsPbCl₃ particles is converted to CsPbI₃ emission. This phenomenon can be utilized in devices containing mixed nanoparticles to avoid complete reabsorption of the blue emission as demonstrated optically in Figure 2. Unfortunately, though, we have not yet been able to fabricate working LEDs with active layer thicknesses below 40 nm.

![Figure 4](image)

**Figure 4.** (a) Band diagram and structure of the bulk heterojunction LEDs. (b) Change in luminance with voltage in the bulk heterojunction LEDs. (c) Electroluminescence spectra of CsPbI₃:PVK, CsPbCl₃:CsPbI₃:PVK, and CsPbCl₃:PVK at different voltages. The electroluminescence spectra of the CsPbI₃:PVK and CsPbCl₃:CsPbI₃:PVK remain constant with voltage (not shown).

In conclusion, we present the study of interactions in blends films with mixtures of different CsPbX₃ (X = Cl, I) perovskite nanocrystals. We find that CsPbCl₃ and CsPbI₃ nanocrystals can exist as discrete entities in solution, embedded in a polymer matrix and as neat films. The CsPbCl₃ emission can be reabsorbed by the CsPbI₃ nanocrystals due to the large absorption coefficient of the CsPbI₃ nanocrystals in the range of the CsPbCl₃ emission. This phenomenon can be utilized in...
bulk heterojunction LEDs where the luminance of devices emitting in the 695 nm region can be improved by the incorporation of CsPbCl₃ nanocrystals. This causes the devices to operate at a higher current density with photon reabsorption transfer occurring from the CsPbCl₃ nanocrystals to the CsPbI₃ crystal for efficient re-emission.

■ ASSOCIATED CONTENT

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Figure S1: Measured absorbance and modeled absorbance spectrum of the mixed 1:1 solutions. Figure S2: Photoluminescence quantum efficiency of different CsPbCl₃:CsPbI₃ blend ratios in PMMA. Figure S3: Powder X-ray diffraction pattern of different CsPbCl₃:CsPbI₃ blend ratios in PMMA. Figure S4: Two different HAADF and EELS TEM scans of different regions. Figure S5: Transient decays for different nanocrystal polymer films excited at 405 nm and measured at 450 and 670 nm. Figure S6: Solution absorbance and emission of CsPbCl₃:CsPbI₃ blends in hexane. Figure S7: Monte Carlo simulations of emission spectra from different nanocrystal solutions with different CsPbCl₃:CsPbI₃ ratios. Figure S8: External quantum efficiencies of LED devices and current density/voltage characteristic of LED devices (PDF)

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N.J.L.K.D. synthesized and characterized the nanocrystals and carried out all experiments unless mentioned otherwise. M.T. and J.R. performed the transient photoluminescence measurements. E.B. performed the XRD measurements. S.M.M. performed the PLQE measurements. F.W.R.R., F.P.M, J.G., and C.D. performed the TEM measurements. R.D.L. carried out the Monte Carlo simulations. N.J.L.K.D., F.D., and N.C.G. contributed to writing the manuscript. All authors contributed to discussion and analysis of the results.

Notes
The authors declare no competing financial interest.

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