Photon Reabsorption in Mixed CsPbCl$_3$:CsPbI$_3$ Perovskite Nanocrystal Films for Light-Emitting Diodes


Supporting Information

ABSTRACT: Cesium lead halide nanocrystals, CsPbX$_3$ (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 CsPbX$_3$ (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 CsPbCl$_3$ to CsPbI$_3$ 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$^{1−17}$ have seen encouraging development as inexpensive absorber layers in solar cells, and show high mobility,$^{18−20}$ bright emission,$^{21}$ tunable band gap,$^{22−24}$ and photon recycling.$^{25}$ Power conversion efficiencies for perovskite solar cells have exceeded 20%.$^{23−26}$ While the majority of research has focused on thin-film and bulk materials,$^{4,15,17}$ perovskite nanocrystals have recently been synthesized. These include hybrid organic–inorganic MAPbX$_3$ (MA = methylammonium, X = Cl, Br, I) nanocrystals and nanostructures as well as all-inorganic cesium lead halide CsPbX$_3$ (X = Cl, Br, I) and cesium tin halide CsSnX$_3$ (X = Cl, Br, I) nanocrystals and nanostructures.$^{26−28}$ 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,$^{19,21}$ 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.$^{2,23}$ As gain media for optically pumped lasers,$^{10,24−28}$ and as emission layers for light-emitting diodes (LEDs).$^{2,29}$

It has been reported that in perovskites ABX$_3$ (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.$^{30}$ The ability of the halide ions to migrate within bulk perovskite has been reported both for MAPbX$_3$,$^{31,32}$ and for CsPbX$_3$,$^{33,34}$ which has specifically been identified as a halide-ion conductor.$^{33}$ 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.$^{35}$ In CsPbX$_3$ 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.$^{33,34}$ Halide exchange has been shown to be possible in both MAPbX$_3$ and CsPbX$_3$ when moving between periodically adjacent halides, for example, from CsPbCl$_3$ to CsPbBr$_3$ and CsPbBr$_3$ to CsPbI$_3$ and vice versa.$^{33,34}$

Although recently there has been an increase in the application of CsPbX$_3$ nanocrystals,$^{24,37−40}$ the inability of CsPbX$_3$ 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 CsPbBr\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 and CsPbI\textsubscript{3} 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.

\section*{Methods}

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

\textbf{Synthesis of CsPbX\textsubscript{3} (X = Cl, I) Nanocrystals.} Perovskite nanocrystals were synthesized using previously reported procedures.\textsuperscript{19} Cs\textsubscript{2}CO\textsubscript{3} (0.814g, 99.9%) was loaded into 100 mL three-neck flask along with oleic acid (ODE, 30 mL, 99%) and oleic acid (2.5 mL, OA, 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 PbBr\textsubscript{2} (0.675g, 99.99%) were loaded into a 250 mL three-neck flask and dried under vacuum for 2 h at 120 °C. After complete solubilization of the PbX\textsubscript{2}, water, the temperature was raised to 170 °C and the Cs–oleate solution (6.0 mL, 0.125 M in ODE, prepared as described above) was quickly injected. After 10 s, the reaction mixture was cooled in an ice–water bath. For CsPbCl\textsubscript{3} synthesis, 5 mL of trioctylphosphine (TOP, 97%) was added to solubilize PbCl\textsubscript{2}. The nanocrystals were transferred to an argon-gloved box (H\textsubscript{2}O and O\textsubscript{2} < 1 ppm) and precipitated from hexane. The nanocrystal dispersion was centrifuged at 10 000 rpm for 60 s, or for polymer samples a 10 mg mL\textsuperscript{-1} perovskite nanocrystal dispersion in 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.

\textbf{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.

\textbf{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.

\textbf{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 were 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 Enfried E 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{37} The EELS data analysis and elemental quantification were performed using the open source software package HyperSpy toolbox.

\textbf{X-ray Diffraction (XRD).} Perovskite nanocrystal films were prepared by drop-casting 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 K\textalpha\textsubscript{r} radiation source (\lambda = 1.5418 Å). The measurements were taken from 2\theta of 10°–70° with a step size of 0.010° in 2\theta.

\textbf{Film Thickness.} Film thicknesses were measured using a DEKTAK profilometer and a Digital Instruments/Veeco Dimension 3100 atomic force microscope.

\textbf{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}

\textbf{LED Device Fabrication.} Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) was spin-coated onto an indium–tin oxide (ITO)-coated glass substrate at 6000 rpm for 45 s, followed by annealing at 140 °C for 30 min in a nitrogen-filled glove box. A 10 mg mL\textsuperscript{-1} perovskite nanocrystal dispersion in 10 mg mL\textsuperscript{-1} PVK in toluene was spin-coated at 2000 rpm for 60 s in an argon-filled glove box to give a 50–60 nm film. The samples were then transferred into a thermal evaporator, and calcium (Ca; 20 nm) and silver (Ag; 80 nm)
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.\textsuperscript{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° and 32.5° corresponding to those found in pure CsPbCl$_3$ crystals reported by Protesescu et al.\textsuperscript{19} and similarly at 14° and 28° 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 ± 2.8 and 12.0 ± 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

![Figure 1](image-url)

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.\(^4\) 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. CsPbCl\(_3\) nanocrystals emit in the near UV at 425 nm, whereas CsPbI\(_3\) 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 \(\approx\) 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 \(\leq\) 10\%) amount of CsPbBr\(_3\) nanocrystals in a solution of CsPbCl\(_3\) and CsPbI\(_3\) nanocrystals. As there is not enough CsPbBr\(_3\) to represent a majority, the CsPbBr\(_3\) is incorporated into the CsPbCl\(_3\) and CsPbI\(_3\) crystals, resulting in a CsPbCl\(_{(1-x)}\)Br\(_x\) and CsPbI\(_{(1-x)}\)Br\(_x\) blend (Figure 2c).

When the crystals were excited directly at 550 nm, the overall PLQE yield of the CsPbI\(_3\) crystals decreased with increasing CsPbCl\(_3\) 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 migration of chloride ions into the CsPbI\(_3\) 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 CsPbI\(_3\) fluorescence decay lifetimes are shortened for ratios greater than 1:1. We are still able to achieve high PLQEs in the CsPbI\(_3\) nanocrystals at a 1:1 ratio.

The above spectra (Figure 2a,b) showed emission from both CsPbCl\(_3\) and CsPbI\(_3\) nanocrystals; however, when CsPbCl\(_3\) and CsPbI\(_3\) nanocrystals are mixed in a 1:1 ratio at higher solution concentrations and in thicker polymer matrices, the emission was found to be predominantly at 695 nm under 405 nm excitation. Solutions of CsPbCl\(_3\) and CsPbCl\(_3\) nanocrystals showed emission solely from the CsPbI\(_3\) crystals up until a 20-fold excess of CsPbCl\(_3\) (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 \(\approx\) 75 nm (Figure 3a). These results indicate that there is efficient energy transfer to the low-energy nanocrystals.
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 the 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 than 0.04% (Figure 8a of the Supporting Information), and relatively high voltages were required to achieve significant luminescences (Figure 4b). Devices containing PVK showed broad emission, consistent with previous reports, and had the highest current densities (Figure 8b). Adding CsPbCl₃ particles had only a minor effect on the current density (Figure 8b), but at high voltages led to a clear emission peak around 400 nm (Figure 4c), consistent with charge capture and recombination occurring on the particles. With CsPbI₃ particles, the emission was solely from the particles, centered around 695 nm (Figure 4c), but the current density was reduced by an order of magnitude (Figure 8b), consistent with trapping of one or both carriers on the particles. Mixed CsPbCl₃:CsPbI₃/PVK devices maintain the high current densities comparable to those of the PVK and CsPbCl₃/PVK devices but show emission solely from the CsPbI₃ nanocrystals (Figure 4c; Figure 8b of the Supporting Information). This suggests that transport is dominated by the CsPbCl₃ particles but that any emission occurring from the CsPbCl₃ particles is converted to CsPbI₃ emission through photon reabsorption as demonstrated in the optical measurements described above. Devices containing mixed nanoparticles therefore show the best device performance. It would be attractive to obtain a mixture of blue and red emission in LEDs, which would require thinner films of 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.

CONCLUSION

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 CsPbCl\textsubscript{3} nanocrystals. This causes the devices to operate at a higher current density with photon reabsorption transfer occurring from the CsPbCl\textsubscript{3} nanocrystals to the CsPbI\textsubscript{3} crystal for efficient re-emission.

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**References**


