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Communication

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Photoinduced Anion Exchange in Cesium Lead Halide Perovskite Nanocrystals

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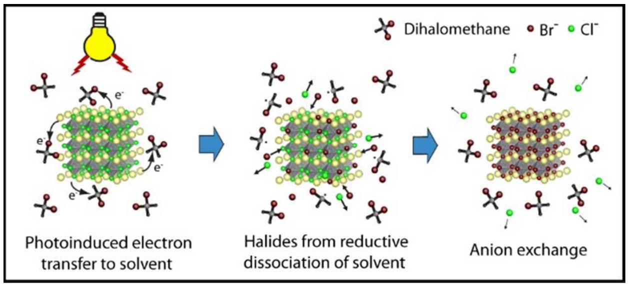
Supporting Information Placeholder

ABSTRACT: Cesium lead halide ($CsPbX_3$) perovskite nanocrystals (NCs) possess the unique capability of post-synthesis anion exchange providing facile tunability of the optical properties, which is usually achieved by mixing NCs with reactive anion precursors. In this work, we show that the controllable anion exchange can be achieved in a dihalomethane solution of $CsPbX_3$ NC in the absence of any spontaneously reacting anion source using photoexcitation of $CsPbX_3$ NCs as the triggering mechanism for the halide ion exchange. The reaction begins with the photoinduced electron transfer from $CsPbX_3$ NCs to dihalomethane solvent molecules producing halide ions via reductive dissociation, which is followed by anion exchange. The reaction proceeds only in the presence of excitation light and the rate and extent of reaction can be controlled by varying the light intensity. Furthermore, the asymptotic extent of reaction under continuous excitation can be controlled by varying the wavelength of light that self-limits the reaction when light becomes off-resonance with the absorption of NCs. The light-controlled anion exchange demonstrated here can be utilized to pattern the post-synthesis chemical transformation of $CsPbX_3$ NCs, not readily achievable using typical methods of anion exchange.

The ability of colloidal $CsPbX_3$ perovskite NCs to undergo rapid anion exchange reactions in solution phase has opened the doors to many interesting applications of these materials. A broad range of tunable photoluminescence (PL) from $CsPbX_3$ NCs could be obtained via a simple post-synthesis procedure, where mixing the solution of NCs with the reactive anion precursors results in the formation of the anion-exchanged NCs with tunable bandgap[1-3] for perovskite nanostructures of various morphologies.[4-6] The labile nature of the halide anions in the perovskite system is generally accepted responsible for their facile exchange in perovskite NCs and other processes involving ion transport, such as long-range anion diffusion under weak perturbation[7,8] and the phase segregation in the methylammonium lead mixed halide system.[9] Several recent studies investigated methylammonium lead iodide/bromide films and $CsPbX_3$ colloidal solutions to understand the nature of anion transport and exchange of halide ions in perovskites of various phases.[10,11] Due to the simple and wide tunability of the photophysical properties of perovskite NCs, anion exchange has been extensively explored using various sources of anions for different applications.[12,13] In most of these cases, the precursors possessed high reactivity to undergo spontaneous anion exchange reaction upon contact with the NCs and the extent of reaction was usually controlled by stoichiometrically limiting the reactant.

In this work, we report the photoinduced anion exchange in solution of $CsPbX_3$ (X=Cl, Br) NCs suspended in dihalomethane, where the extent of the anion exchange reaction and its rate are controlled by the intensity or wavelength of light without using any reactive sources of halide. In our study, dihalomethane molecules that normally function as the unreactive solvent produce halide ions via photoinduced electron transfer from $CsPbX_3$ NCs resulting in reductive dissociation of the solvent molecules. The halide ions generated in-situ near the surface of NCs drive the anion exchange reaction efficiently, as long as the $CsPbX_3$ NCs are photoexcited above the bandgap. The proposed mechanism of the photoinduced anion exchange in $CsPbX_3$ NCs is illustrated in Scheme 1. The photoinduced anion exchange in $CsPbX_3$ NCs can give a unique capability not available from the earlier anion exchange reactions, such as spatial patterning with controllable stoichiometry.

Scheme 1. Illustration of the proposed mechanism for photoinduced anion exchange of perovskite nanocrystals.



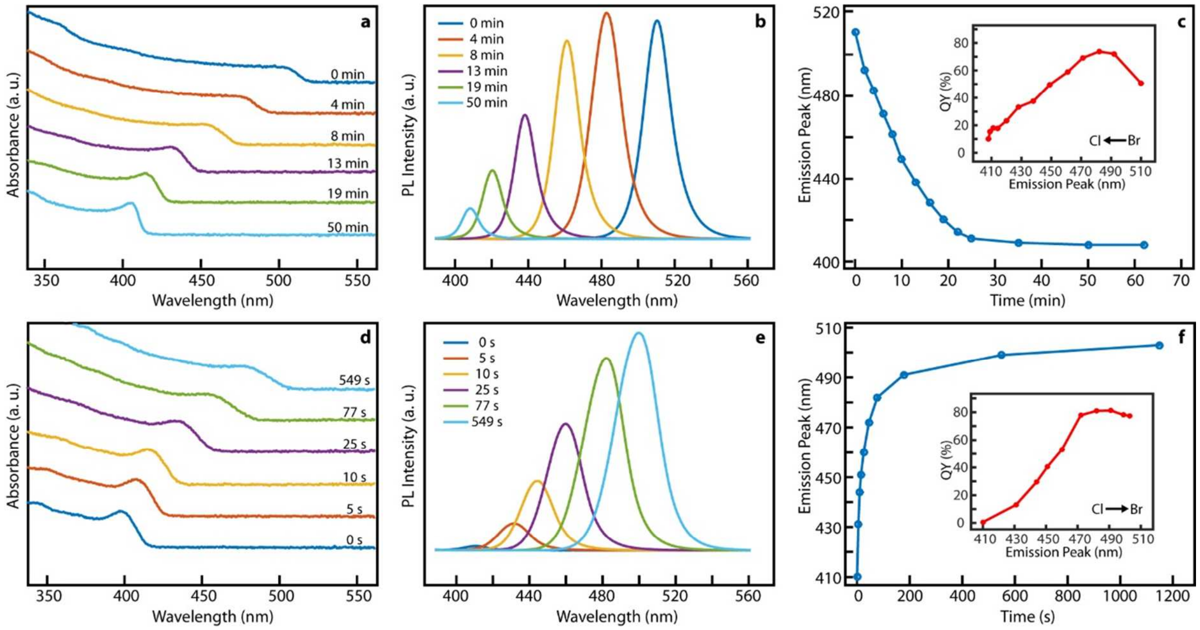


Figure 1. Photoinduced anion exchange of $CsPbX_3$ NCs in dihalomethane solvent. (a,b,c) Time dependence of absorption spectrum (a), PL emission spectrum (b), and PL emission peak (c) for $CsPbBr_3 \rightarrow CsPbCl_3$ in DCM/hexane. (d,e,f) Time dependence of absorption spectrum (d), PL emission spectrum (e), and PL emission peak (f) for $CsPbCl_3 \rightarrow CsPbBr_3$ in DBM/hexane.

We demonstrate the photoinduced anion exchange using dichloromethane (DCM) and dibromomethane (DBM) as the inert solvent that also functions as the locally photoactivatable source of halide anions in the immediate vicinity of the perovskite NCs. $CsPbBr_3$ and $CsPbCl_3$ NCs used in this study were synthesized following a previously reported method[1] with minor modifications. The detailed procedures of $CsPbX_3$ NC synthesis and photoinduced anion exchange reaction, TEM images and X-ray diffraction patterns of the NCs before and after the anion exchange are in the Supporting Information. Figure 1 summarizes the continuous changes of the absorption and emission spectra during the process of photoinduced anion exchange in $CsPbBr_3$ NCs dispersed in mixed solvent of DCM/hexane (Figure 1 a,b) and $CsPbCl_3$ NCs in DBM/hexane (Figure 1 d,e). The time-trace of the PL emission peak and the PL quantum yield correlated with PL emission peak are also shown for both reactions (Figure 1 c,f). The mixture of hexane and dihalomethane was used as the solvent instead of pure dihalomethane for better solubility of the NCs facilitating more accurate measurement of the optical spectra, while the same photoinduced chemistry can be performed in pure dihalomethane. The entire volume of the solution sample contained in a 1 cm-thick cuvette was illuminated with weak 405 nm light (~20 mW/cm^2) to excite the NCs without stirring the solution.

In the absence of photoexcitation in the dark, the absorption and emission spectra were constant over time, indicating that no anion exchange occurs in the solution of $CsPbCl_3$ and $CsPbBr_3$ NCs in their respective dihalomethane/hexane solvent (See Supporting Information). Upon illumination with 405 nm light, $CsPbBr_3$ NCs in DCM/hexane showed a blueshift of both absorption and emission spectra indicating the exchange of bromide with chloride. Similarly, $CsPbCl_3$ NCs in DBM/hexane showed a redshift of the spectra from the exchange of chloride with bromide. This indicates that the exchange of anions can occur in both directions and that the direction of the reaction can be varied by changing the solvent composition. The PL quantum yield, shown as insets in Figure 1 c,f, generally decreases with increasing Cl content in $CsPb(Cl/Br)_3$ mixed halide NCs for the anion exchange reaction in both directions, consistent with earlier observations.[2,3] In order to confirm that the exchange between the two different halide ions is the direct result of light absorption by perovskite NCs, the progress of the reaction was monitored by changing both the intensity and wavelength of the excitation light. Figure 2a shows the shift of the PL emission peak with alternating 'on' and 'off' periods of the photoexcitation for the anion exchange reaction of $CsPbBr_3$ NCs in DCM/hexane. The shift of the PL emission peak occurs only during the 'on' period, indicating that the extent of reaction can be precisely controlled with photon dose. In addition, the rate of reaction could also be controlled by varying the intensity of light (See Supporting Information), indicating that the rate of production of halide ions via photoexcitation is the main rate limiting step for the overall exchange reaction.

The essential role of photoexcitation of the perovskite NCs in anion exchange is further demonstrated in the 'self-limiting' behavior of the reaction when the excitation light becomes off-resonance with the absorption of the perovskite NCs during the exchange process. Figure 2b compares the PL emission peak shift from the anion exchange of $CsPbBr_3$ in DCM/hexane under excitation at 405 and 445 nm. When 445 nm light is used, the reaction stops near the PL emission peak of 440 nm due to the inability of the NCs to absorb light, in contrast to the case of 405 nm excitation that results in a nearly complete anion exchange. This demonstrates that the extent of reaction can be controlled also with the wavelength of the excitation light in addition to the photon dose. Furthermore, two-photon excitation of the perovskite NCs at 800 nm, where there is no linear absorption in solution, could induce the anion exchange (See Supporting Information), suggesting an interesting possibility of photo patterning even in 3-dimensions, with an appropriate medium that limits the diffusion of the NCs and solvent. The above observations demonstrate the unique benefits of the photoinduced anion exchange reaction in gaining precise post-synthesis control of the perovskite NCs bandgap.

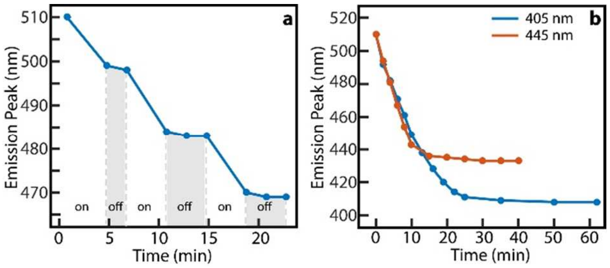


Figure 2. PL emission peak shift for $CsPbBr_3$ in DCM/hexane (a) under ‘on’ and ‘off’ period of excitation light (b) under two different excitation wavelengths, 405 and 445 nm.

The possible mechanism for the photoinduced anion exchange reaction is the dissociation of the reduced solvent molecules via interfacial electron transfer from the photoexcited perovskite NCs. Most alkyl halides are known to undergo concerted reductive dissociation into halide ion and alkyl radical under both heterogeneous (e.g., electrochemical) and homogeneous reduction conditions.[14,15] The reduction potential of various alkyl halides are less negative than -1V vs SCE (saturated calomel electrode) in common organic solvents.[16] Therefore, the reduction can be achieved via interfacial electron transfer from the conduction band of $CsPbX_3$ NCs that are energetically located above the reduction potential. For instance, the conduction band edge of $CsPbBr_3$ measured electrochemically[17] and from ultraviolet photoelectron spectroscopy,[18] is 3.35 eV below vacuum level, which is sufficient to reduce DCM that has a reduction potential of -1.04 V vs SCE corresponding to 3.7 eV below vacuum level (See Supporting Information). From the interfacial electron transfer to solvent molecules, halide ions should be produced in the immediate vicinity of the NCs creating a relatively high local concentration which should facilitate the exchange reaction. This scenario is also corroborated by the observation of the slower reaction rate when the solution is rapidly stirred, which can be attributed to the reduced local concentration of the photogenerated halide ions near the surface of NCs. The holes remaining on NCs should ultimately be removed to continue the reaction and this may involve back electron transfer from remaining halide ions. The detailed understanding of the fate of holes and other organic species is beyond the scope of this study and will be addressed in a later work.

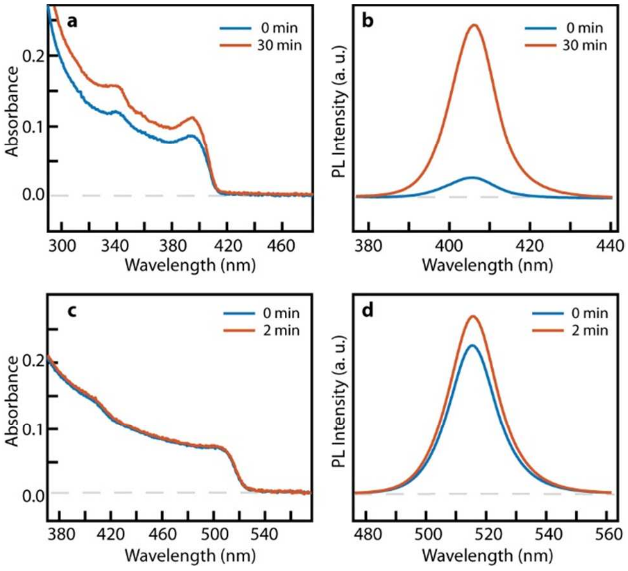


Figure 3. (a,b) Absorption and PL emission spectra before and after excitation of $CsPbCl_3$ NCs in DCM/hexane. (c,d) Absorption and PL emission spectra before and after excitation of $CsPbBr_3$ NCs in DBM/hexane.

For the two anion exchange reactions shown in Figure 1, the absorbance of $CsPbX_3$ NCs at the excitation wavelength and light intensities are comparable. However, the rate of reaction is an order of magnitude faster for $CsPbCl_3$ to $CsPbBr_3$ in DBM/hexane than $CsPbBr_3$ to $CsPbCl_3$ in DCM/hexane. This may be explained from the combination of the differences in the reduction potential of the solvent molecules and conduction band edge of $CsPbX_3$ NCs rather than photon absorption rate per each NC dictated by the absorption cross section. For alkyl halide molecules, the reduction potential of bromide is less negative than chloride.[16] Furthermore, the conduction band edge of $CsPbCl_3$ is higher than that of $CsPbBr_3$. Therefore, one would expect more facile electron transfer from $CsPbCl_3$ to DBM than from $CsPbBr_3$ to DCM, resulting in a large difference in the rate of halide ion production. In the case of chloromethane series, teterachloromethane showed a faster photoinduced anion exchange reaction than DCM. This may be partially due to the lower reduction potential promoting the faster electron transfer. It is worth to mention that photoinduced anion exchange is less controllable in trihalomethane because of the potentially higher concentration of the reactive contaminants that can be produced under light exposure, resulting in the partial anion exchange even in the absence of light.

When $CsPbBr_3$ and $CsPbCl_3$ NCs are photoexcited in solvent containing their respective halide, i.e., DBM and DCM, there is no net exchange of halides. However, a significant enhancement of PL quantum yield was observed especially in $CsPbCl_3$, typically exhibiting low PL quantum yield (~1%) when freshly synthesized.[3] The absorption and PL emission spectra before and after the photoinduced exchange of the same anion are shown in Figure 3. In the case of $CsPbCl_3$ NCs, the PL quantum yield increases by an order of magnitude (~1%→~10%) accompanied by a substantial increase of the absorption intensity (Figure 3 a,b). In the case of $CsPbBr_3$ NCs that already exhibit 60-80% PL quantum yield when freshly synthesized, the increase of PL quantum yield is ~10% with negligible change in the absorption intensity (Figure 3 c,d). This observation suggests one possible origin of particularly low PL quantum yield in $CsPbCl_3$ NCs and the potential role of photoinduced ‘self-anion exchange’. The lower PL quantum yield of $CsPbCl_3$ compared to $CsPbBr_3$ could occur from the relatively high concentration of halide vacancies which could be removed through photoinduced self-anion exchange. The increase of the absorption intensity may reflect the filling of vacancies that increases the density of states involved in the optical absorption. Further confirmation of the above hypothesis will require additional work on the measurement of the optical absorption cross section and accurate elemental analysis.

In a separate experiment, we tested whether the anion exchange reaction can be performed without directly exciting the perovskite NCs by using a separate species that can transfer the electron to the solvent molecules. For this purpose, we examined the anion exchange reaction in the mixture of $CsPbCl_3$ NCs and CdSSe/ZnS core/shell quantum dots dispersed in DBM/hexane under 445 nm excitation, where only CdSSe/ZnS quantum dots absorb light. Figure 4 compares the result from this measurement with that from the reaction of $CsPbCl_3$ NCs under 405 nm excitation, where the average photon absorption rates in the two sample solutions were kept similar. As expected, the mixture of $CsPbCl_3$ NCs and CdSSe/ZnS can also undergo anion exchange reaction, although the rate is slower likely due to the lower local anion concentration near the surface of the perovskite NCs.

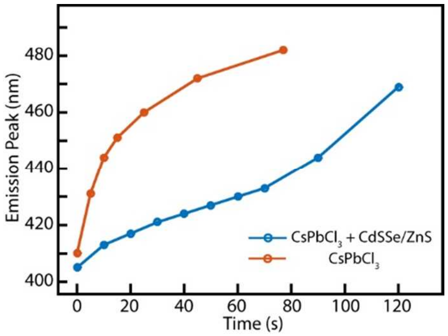


Figure 4. Comparison of the photoinduced anion exchange reactions occurring from the excitation of $CsPbCl_3$ NCs (orange curve) and excitation of CdSSe/ZnS quantum dots (blue curve) in the mixture of $CsPbCl_3$ NCs and CdSSe/ZnS quantum dots.

In summary, we have shown a highly controllable method of anion exchange using light as the triggering mechanism in the solution of $CsPbX_3$ NCs dispersed in dihalomethane. In-situ production of halide anions via reductive dissociation of the solvent molecules following the interfacial electron transfer from the photoexcited $CsPbX_3$ NCs is considered as the mechanism for the photoinduced anion exchange. We were able to control the extent of anion exchange reaction precisely by controlling either photon dose or wavelength of the excitation light. Multiphoton excitation was also able to induce the anion exchange, creating the potential use for photo patterning in a viscous medium. The self-exchange of the same anions, particularly in $CsPbCl_3$ NCs, resulted in an order of magnitude increase of the PL quantum yield, which may have resulted from the removal of the anion vacancy. The high level of control of the rate and extent of anion exchange reaction and the potential to spatially pattern the chemical transformation with light will be valuable for the post-synthesis modification of perovskite NCs for various applications.

ASSOCIATED CONTENT

Supporting Information

The synthetic procedure, experimental details, TEM and XRD patterns of the nanocrystals, PL shift from anion exchange under varying excitation intensity and under two photon excitation conditions are provided in the supporting information and can be found free of charge on the ACS publication website.

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Notes

The authors declare no competing financial interests.

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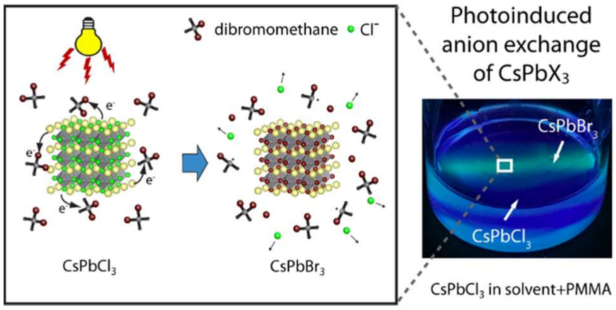
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$CsPbBr_3$
Photoinduced anion exchange of $CsPbX_3$
$CsPbBr_3$
$CsPbCl_3$
$CsPbCl_3$ in solvent+PMMA