***Using Perovskite Nanoparticles as Halide Reservoirs in
Catalysis and as Spectrochemical Probes of Ions in Solution***

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Catalysis and as Spectrochemical Probes of Ions in Solution*

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Abstract: The ability of cesium lead halide CsPbX₃ (X= Cl⁻, Br⁻, I⁻) perovskite nanoparticles (P-NPs) to participate in halide exchange reactions, to catalyze Finkelstein organohalide substitution reactions, and to colorimetrically monitor chemical reactions and detect anions in real time is described. Using tetraoctylammonium halide salts as a starting point, halide exchange with the P-NPs was performed to calibrate reactivity, stability, and extent of ion exchange. The exchange of CsPbI₃ with Cl⁻ or Br⁻ causes a significant blue-shift in absorption and photoluminescence, whereas reacting I⁻ with CsPbBr₃ causes a red shift of similar magnitudes. With the high local halide concentrations and the facile nature of halide exchange in mind, we then explored the ability of P-NPs to catalyze organohalide exchange in Finkelstein like reactions. Results indicate that the P-NPs serve as excellent halide reservoirs for substitution of organohalides in non-polar media, leading to not only to new organohalides, but also a complementary color change over the course of the reaction, which can be used to monitor kinetics in a new and precise manner. The merits of using P-NP as spectrochemical probes for real time assaying is then expanded to other anions which can react with, or form new, classes of perovskites.

Keywords: Nano, Perovskite, CsPbX_3 , Lead Halide, Anion Exchange, Chemical Assay, Finkelstein, Colorimetric, Spectrochemical

TOC Graphic:

Nanoparticles are known for size-, shape- and composition tunable optical properties which often exceed those of molecular counterparts.¹⁻⁷ Tuning is often achieved at the point of synthesis by varying concentrations, reactions times, ligand or surfactant mixtures, and temperature.¹ Once tuned, these properties are typically static, and exposure to varied environmental conditions after synthesis lead to only minimal changes, such as fluorescence quenching in quantum dots⁸ or plasmon shifts in metal nanoparticles.^{9,10} Additional reaction or processing steps can be performed post-synthesis to adjust properties, but examples of reactions that induce significant optical change are limited to those like ion exchange of quantum dots,¹¹ or the galvanic exchange of metal nanoparticles.¹² One emerging class of materials that show promise for a broader diversity of optical changes are perovskites, which have great promise in photovoltaics as thin films and bulk solids.^{13,14,15} Recently, perovskite nanoparticles (P-NPs) were synthesized at the nanoscale with remarkable size and halide-tuned optoelectronic properties.^{16,17} Of interest to the synthetic chemist is the seemingly ease of which P-NPs undergo composition change by exchange with halides, as shown at bulk-¹⁸ and at nano-interfaces.¹⁹⁻²¹ While nascent, current focus of P-NPs is on developing the next generation photovoltaics and optics, but there may exist great potential for use in new paradigms of spectrochemical sensing, colorimetric monitoring of reactions, and as catalysts in synthesis.

Herein, we describe the use of cesium lead halide (CsPbX_3 , $\text{X} = \text{I}^-$, Br^- , Cl^-) P-NPs to actively react with organohalides during exchange reactions, to colorimetrically monitor reactions in real time, and to assay ions in solution. The extent and feasibility of halide exchange is first probed using a number of tetraoctylammonium (TOA) based halide salts. We then explore the ability of the P-NPs to act as halide reservoirs for Finkelstein exchange reactions in organohalides, which provide a unique colorimetric readout of reaction kinetics. A general mechanism for halide exchange and Finkelstein reactivity is discussed in light of phase transfer behavior, and then expand to other monovalent anions.

RESULTS AND DISCUSSION

The CsPbX_3 P-NPs used in this study were synthesized according to the recent method by Kovalenko and co-workers.¹⁶ Figure 1 shows a summary of the P-NPs makeup and properties. The P-NPs have a cube shapes, and are capped with a mixture of oleylammonium halide and oleylammonium oleate (a),²² which are derived from oleylamine (OAm) and oleic acid (OAc) used in synthesis. Transmission Electron Microscopy (TEM) was used to determine size (b) of a $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ P-NP, which had a distorted cube shape, where the shorter length (l) is 11.5 ± 2.1 nm, and the longer length is 13.9 ± 2.8 nm. The CsPbI_3 and CsPbBr_3 , were more spherical and had sizes of 15.0 ± 3.6 and 10.4 ± 1.3 nm respectively (Fig. S1). Powder X-ray diffraction (XRD) confirmed a cubic perovskite crystal structure and Scherrer broadening consistent with the sizes (c). Varying Br^- and I^- concentrations during synthesis yielded optically distinct materials, as shown in (d). For example, CsPbBr_3 and CsPbI_3 has PL emission at ~ 510 and ~ 680 nm, respectively, while the mixed composition $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ was in between. The P-NPs had quantum yields (QY) of $\approx 42\text{-}44\%$, and long single exponential PL lifetimes on the order of >20 ns (Fig. S2).¹⁶ Additionally, the QY was stable even at temperatures up to 50°C , where only a

~20% drop in QY was observed, and resulted in a total loss of only ~5% upon cooling (Fig. S3).

Unless otherwise noted, all studies were performed in air and moisture free environments, with the P-NPs dispersed in dry hexane under N₂ or Ar atmospheres.

Figure 1. (a) Schematic illustration of the P-NPs, which had halide-tunable compositions, and were capped with a mixture of oleylammonium halide and oleylammonium oleate. (b) Representative TEM micrograph of CsPbBr_{1.5}I_{1.5} NPs with average width of 11.5 ± 2.1 nm. (c) Powder XRD of CsPbBr₃ NPs revealing cubic perovskite crystallinity. (d) Characteristic UV-vis (solid line) and PL spectra (dashed line) for CsPbX₃ at X = Br⁻ (blue), I⁻/Br⁻ (orange) and I⁻ (red).

We first studied the halide exchange of P-NPs using tetraoctylammonium (TOAX, X = Cl⁻, Br⁻, I⁻) based salts. The halide exchange was monitored by absorption (UV-vis) and photoluminescence (PL) spectroscopy. Figure 2a shows a schematic of this process. When CsPbCl₃ is reacted with excess TOABr, a red-shift in UV-vis and PL is observed. In contrast, reacting CsPbI₃ with TOABr, results a blue-shift. This process is best-described using visuals, and (b) shows a photograph of these halide exchange reactions at different TOABr

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concentrations. The corresponding PL-shifts are quantified in (c). These exchanges were also reversible (Fig. S4). In general, we found that using TOACl that Cl^- will also substitute for I^- in CsPbI_3 , but the resulting CsPbCl_3 were not observed to revert upon treatment with TOAI (Fig. S5), indicating that the CsPbCl_3 P-NP is particularly stable.¹⁸ The results correlate to the stability of the cubic perovskite as given by the Goldschmidt factor,¹³ where transition from I^- to Br^- to Cl^- results in an increasingly stable cubic lattice, and is largely responsible for the inability to form CsPbI_3 from CsPbCl_3 . It's important to note that these trends have been observed by other researchers^{19–21} and is supported by reaction enthalpy calculations in the synthesis of methyl ammonium (MA) lead halide perovskites (MAPbX_3).²³ The results here demonstrate the further ability to use TOAX salts in halide exchange or synthesis.

Figure 2. (a) Schematic of P-NP halide using TOAX salts ($X = \text{Cl}^-$, Br^- , I^-). (b) Photograph of PL shift during the halide exchange of CsPbCl_3 (left) and CsPbI_3 (right) with increasing concentrations of TOABr in hexane, accompanied with corresponding PL spectra.

It is interesting to note the difference in final composition of the exchanged P-NPs, as judged by PL in Figure 2c (middle panel). The difference between the conversion CsPbCl_3 or CsPbI_3 P-NPs to CsPbBr_3 is considerable, even using smaller TOABr ratios resulted in near instantaneous color change in CsPbI_3 P-NPs with only minor change to CsPbCl_3 P-NPs (Fig. S6-S7). This suggests interplay of halide equilibrium and exchange thermodynamics is critical for inducing halide exchange. Selectivity constants, the ratio of two equilibrium constants, for the phase transfer of Br^- and I^- relative to Cl^- by quaternary salts into toluene from aqueous solution, for instance, have been reported to be 16.5 and 5000, respectively.²⁴ Similarly, distribution ratios

of anion water/chloroform partitioning in the presence of a phosphonium phase transfer agent²⁴ relative to Cl^- show an enhanced partitioning of 19 and 300 for Br^- and I^- respectively. Thus, in addition to the thermodynamic penalty for exchanging Cl^- with Br^- , the stability of the resulting TOAX salt must also be considered when assessing the extent to which exchange will occur. The role of free halide equilibrium was confirmed when as-synthesized red emitting CsPbI_3 were converted to yellow emitting $\text{CsPbBr}_x\text{I}_{1-x}$ P-NPs using TOABr, but transformed to either CsPbBr_3 or CsPbI_3 when diluted with solvents of different dielectric constants (Fig. S8). Importantly, the data also suggests that halide exchange is less detrimental to the P-NP photophysical properties when conducted in more polar environments (Fig. S9).

After observing the dynamics of halide exchange, the ability of the P-NPs to exchange high percentages of halides while remaining intact, and the resulting colorimetric response, we hypothesized that P-NPs may be able to; (1) serve as a source of high concentrations of halides in non-polar media (*i.e.*, catalytic reservoir),²⁴ (2) monitor free halide concentration change during organohalide elimination reactions,²⁵ and (3) serve as a rapid qualitative/quantitative colorimetric assay of free ions in solution. Figure 3 illustrates these ideas. As a halide reservoir (a), the P-NP and its dynamic halide-ligand complex²² sources halides in non-polar media which can react and exchange with organohalides, while at the same time providing colorimetric feedback. As an assay (b), sampled reactions (organohalide elimination or substitution) or unknown ions are introduced to P-NPs aliquots of known concentration whose color change can provide quantitative colorimetric response. And when combined, route a and b can provide a new approach towards colorimetric monitoring chemical reactions in real time.

Figure 3. Schematic illustration of P-NPs as halide reservoir and colorimetric probes. The P-NPs can serve as a halide source in Finkelstein reactions of organo-bromides. In the present systems, CsPbI_3 are exchanged with organic-bromides, forming organo-iodides and CsPbBr_3 (a). In addition, similar reactivity use used to assay organohalide based chemical reactions, where released Br^- during the course of a reaction can be observed by colorimetric change of the P-NP.

As a proof-of-principle we investigated using P-NPs as halide reservoirs for halide exchange in organohalides. These reactions, often referred to as Finkelstein reactions,²⁴ occur when the halide components of an organohalide are exchanged, and are critical when preparing organohalides of tailored reactivity and selectivity, which are used as building blocks in a wide array of synthetic organic reactions.²⁶ One challenge in these is the difficulty in having high local concentration of halides in non-polar media. Traditionally, phase transfer catalysts accomplish this, but reactivity varies depending on solvent conditions (as described above) and other reactive molecules present. As illustrated in Figure 3a, the P-NP solubility and high local halide concentrations may allow for improvements in these reactions by participating directly as halide reservoirs. Other molecules present in the reaction, and also the stabilizing ligand of the P-NPs

may also influence the reaction (see below).²⁷ Interestingly, the result of this reaction should induce a complementary P-NP halide exchange as well, leading to a convenient colorimetric response like that shown in Figure 2.

Figure 4. (a) Representative PL spectra of CsPbI₃ during reaction with 2-Br. Inset: Correlation of the PL wavelength shift after 75 min. reaction with 2-Br over a range of 2-Br concentrations. ([CsPbI₃] ~15 µg/mL, [2-Br] = 1 mM, hexane). (b) A photograph of the PL response for a high throughput assay of CsPbI₃ and 2-Br. ([CsPbI₃] ~65 µg/mL, [2-Br] = [OAm], hexane, T = 25 °C). (c) A time lapse series of photographs following a Finkelstein exchange between CsPbI₃ and 2-Br over 90 min (i-v). Both b and c under hand held UV illumination.

To test the halide reservoir hypothesis, we monitored the reaction between CsPbI₃ and 2-bromododecanoic acid (denoted as 2-Br), in the presence of 1 equivalent of octylamine (OA). The reaction was then monitored by PL change using a handheld UV-lamp or fluorescence spectrometer. After a few minutes, a PL change from red to green was observed by eye, which indicated the transformation of CsPbI₃ to CsPbBr₃ (Figure 4c), suggestive of a conversion from

2-Br to 2-iodododecanoic acid (denoted as 2-I). Figure 4a shows the *in-situ* monitoring of the reaction by PL change, in which a systematic wavelength shift ($\Delta\lambda$) of ~140 nm is observed. This blue-shift was found to be linearly dependent on 2-Br concentration (Fig. 4a, inset). As a control, an identical reaction with dodecanoic acid (denoted as DA), which does not have a Br, resulted in no PL shift or color change (Fig. S10). Further, when excess OA was used (allowing for the possibility of an elimination or substitution reaction), no enhancement in $\Delta\lambda$ was observed. In contrast, if the concentration of 2-Br far exceeded that of OA, only a slight $\Delta\lambda$ but dramatic PL quenching was observed (Fig. S11), suggesting that 2-Br and P-NP are interacting directly in those cases. Perhaps most importantly, this chemical change (in both the P-NP and the 2-Br) is easily observable by eye, due to the high quantum yields of the P-NP, and the colorimetric nature of the response (a). Figure 4b shows a well-plate assay under high throughput conditions of increasing total 2-Br concentration, but constant P-NP concentration. At higher concentrations and longer reaction times, the color change from red-to-blue/green is most pronounced, indicative of a more complete reaction. The further quantitative analysis of these results is shown below.

One challenge with this model reaction was the possibility that 2-Br can also undergo a substitution or elimination reaction (forming a alkylamine adduct or alkene, respectively), both of which would release Br^- , which in turn would lead to color change. To investigate this, the reaction was followed by ^1H -NMR. Figure 5a shows typical spectra for controls containing 2-Br + OA in C_6D_6 . Compared to the 2-Br alone, the combination leads to a pronounced ppm shift along with a splitting of the β protons at ~2.3 ppm, the later of which is indicative of carboxylate form of 2-Br (confirmed in a control experiment using CD_3OD , Fig. S12) and former is

suggestive of a stable 2-Br + OA contact pair. Thus, we consider the Finklestein reaction is occurring with this stable 2-Br + OA contact pair.

Figure 5. (a) Representative ¹H-NMR spectra for 2-Br (red), 2-Br + OA (blue), and CsPbI₃ + 2-Br + OA (green). (b) ¹H-NMR of 2-Br and OA with and without P-NP initially (red) and after 96 h (black) ([2-Br] = [OA] = 2mM). (c) Photograph of NMR tube under UV light during the CsPbI₃ + 2-Br + OA reaction, and (d) of CsPbI₃ and CsPbCl₃ P-NP induced Finkelstein reaction with 2-Br ([2-Br] = [OAm]).

When the P-NPs are present in the reaction (Fig. 5b), the spectra are similar except for new features at 5.5 ppm due to OAm and OAc contributions from the P-NP's encapsulation. Despite a clear PL color change (Fig. 4, 5c), no new features are observed after 96h of reaction in the 2-

Br + OA + P-NP reaction spectra. New ^1H chemical shifts for OA substitution at the α position are expected at ~ 3.6 ppm (R-NH-CH-COOH) and ~ 3.2 ppm (R-NH-CH-COOH),^{28,29} while alkene signatures would be expected at ~ 5.8 ppm when compared to a control spectra of decenoic acid (Fig. S13). Comparison of the NMR spectra of equimolar 2-Br and OA both with and without the P-NP after 96h (Fig. 5b, red traces) confirms that the reaction is due to the P-NP, and the Finkelstein reaction is exclusively occurring in our conditions (Fig. S11). We were able to isolate the 2-I product by scaling to larger volumes of the identical molar ratios, followed by purification *via* silica column and concentration. In this step, the P-NPs were absorbed to the initial silica layers, and thus conveniently separated. NMR analysis (Fig. S14) confirmed ^1H shift from 4.55 ppm in 2-Br, to 4.30 ppm in the 2-I, in good agreement with controls. Interestingly, a similar reaction can occur when using CsPbCl_3 and 2-Br, demonstrating this approaches versatility in creating a number of organohalide types, as shown in Figure 5d.

Figure 6. (a) UV-vis of CsPbI₃ at 32 (i), 65 (ii), and 108 µg/mL (iii). (b) The calibration of colorimetric response ($\Delta\lambda$) of the three CsPbI₃ concentrations (i-iii) calibrated known [TOABr] stocks, revealing linear dependence. Inset: Photograph of TOABr calibration of (i). (c) Quantified kinetic traces revealing extent of Br⁻ exchange between CsPbI₃ and 2-Br at the three [CsPbI₃]. Inset: Typical PL response. (d) Comparison of the total TOABr concentration needed for full conversion of each P-NP concentration (i-iii), to the amount of Br⁻ detected after 2.5 h of reaction (e), indicating that [P-NP] does not alter the reaction rate, where (ii_b) is a repeat experiment of (ii).

Next, the P-NP colorimetric response to halide exchange was quantified and calibrated allowing for accurate kinetic monitoring of the reaction. Figure 6 shows the quantification of the reaction described in Figure 5, where the molar concentration of 2-Br (denoted as [2-Br]) was held constant but reacted with varied concentration of P-NP (denoted as [P-NP]), as shown in Figure 6a. At each of these [P-NP], colorimetric response of PL ($\Delta\lambda$) was first calibrated using TOABr, and these traces are shown in Figure 6b. We found linear responses until nearly all of the I⁻ was exchanged (~90%), after which point the correlation between $\Delta\lambda$ and concentration of Br⁻ (denoted as [Br⁻]) plateaued; we speculate this is related to the TOABr dissociation equilibrium with increasing concentration. Figure 6c plots the kinetic traces after $\Delta\lambda$ is [Br⁻] release *versus* time. The traces deviate from a kinetic behavior related to reactant concentration, especially at early time, showing instead a slow inductive build up before a steady conversion. Figure 6d shows the [Br⁻] necessary for full conversion of the three P-NP concentrations, while Figure 6e shows the conversion after 2.5 h of reaction. Despite a substantial increase in the amount of total I⁻ available in the system, no systematic relationship between [P-NP] and reaction rate is observed. Taking these two observations together, we propose that the P-NP based halide reservoir is able to replenish free I⁻ reactant much faster than the corresponding halide substitution, yielding a pseudo first order rate constant with respect to 2-Br. Ideally, these reactions should proceed with a second order rate dependent on both free I⁻ (from CsPbI₃), and

2-Br, but a pseudo-first order reaction has also been shown when the rate at which free I^- is made available in the non-polar phase is much greater than the rate of halide substitution in phase transfer catalysis.²⁴ As the conversion of CsPbI_3 with TOABr was rapid (see Fig. 2), we hypothesized that during the reaction the colorimetrically determined rate was primarily that of halide substitution at 2-Br. Studies of CsPbI_3 with two other organohalides, 1-bromododecane, and *t*-butyl bromide, resulted in greatly diminished kinetics and yields in agreement with general $\text{S}_{\text{N}}2$ considerations (electron-withdrawing groups and sterics), further emphasizing that we are observing halide exchange at the organohalide (Fig. S15).

Figure 7. A proposed reaction mechanism for P-NP undergoing halide exchange with alkylammonium halides (route 1), and acting as halide reservoirs in Finkelstein halide exchange of organo halides (route 2). For simplicity, R_4N^+ symbolizes the TOA^+ used in route 1 of this study, whereas octylammonium halides derived from octylamine, and 2-bromododecanoic acid were used in route 2.

Figure 7 proposes the mechanism for direct halide exchange between P-NPs and alkylammonium halide salts and halide exchange between P-NP halide reservoirs and organo halides. In route 1 the P-NP is directly exchanged with the alkylammonium halide (Fig. 2). In this system tetraoctylammonium halide salts were used, however other alkylammonium halide

have been used.^{19–21} Due to the high concentration of free halide, and driven by Goldschmidt parameters, exchange is facile ($k_{exchange}$). This is also supported by calculations of anionic movement for bulk CsPbI₃, due to activation energy of ≈ 0.6 eV,³⁰ and as previous bulk ion exchange studies with perovskites have identified this as the limiting step,¹⁸ it is expected that ion diffusion is even more enhanced at the nanoscale.³¹ The main determinant of $k_{exchange}$ then is the overall stability of the P-NP and the alkylammonium halide salt equilibrium, both of which work synergistically to favor smaller anion incorporation. For instance, the enthalpies of formation of CH₃NH₃PbX₃ are -67.5, -24.1, and -9.6 kJ/mol for Cl⁻, Br⁻, and I⁻ perovskites, respectively,²³ and the relative solubility of halide anions in non-polar media increases in the order I⁻ < Br⁻ < Cl⁻,²⁴ the different sensitivities of CsPbCl₃ and CsPbI₃ to TOABr concentration shown in Figure 2 is easily rationalized. Thus unlike most chemical colorimetric probes which rely on specific chemical bond formation, the driving force in this system is largely due to anion size and their solubility in non-polar solvents.

In contrast, as halide reservoirs in (route 2), there exists a more complicated mechanism for halide exchange. The proposed mechanism can be divided into three steps: anions from the P-NP are transported *via* a quaternary ammonium phase transfer agent (step 2a), the transported halide reacts with the halogenated organic compound such as 2-Br (step 2b), and the displaced X⁻ is then exchanged with another X⁻ in the P-NP (step 2c). Although the same criteria for halide exchange in route 1 hold for steps 2a and 2c, the data indicates that the rates measured are dictated by the observed chemical reaction such that $k_{exchange} \gg k_{sub}$. This also is corroborated by the pseudo-first order reaction rate obtained in Figure 6, where k_{sub} was insensitive to [P-NP] in the concentration regime studied. Based on these results, it is clear that the P-NP serves as an ion exchange medium similar to ion exchange resins in phase transfer reactions, opening new

avenues into studying chemical dynamics which can be quantified through colorimetric responses.

Figure 8. UV-vis (a) and PL (b) spectra of CsPbI₃ NPs titrated with indicated anions. (c) Colorimetric assay of NO₃⁻ (left) and ClO₄⁻ (right) in hexane using CsPbI₃ and CsPbBr₃ NPs.

In closing we return briefly to P-NP based assaying, as illustrated in Figure 3b, where we propose a direct exchange or binding of P-NPs with anions, in which the corresponding spectrochemical response could be used as a sensitive and selective optical readout. As the reaction between anions and P-NPs is largely *via* exchange, we investigated the ability of P-NPs to detect non-halide anions in solution, all of which are predicted to retain the cubic lattice structure (see SI, Fig. 16). Figure 8a shows the comparative response of CsPbI₃ when exposed to NO₃⁻ and BF₄⁻ anions in non-polar solvent. Both NO₃⁻ and BF₄⁻ quench P-NP PL (b), and new absorption at high energy are observed (a). At this time it is not apparent as to the extent of NO₃⁻ or BF₄⁻ exchange, however powder XRD observed only minor <100> reflections change after

reacting (Fig. S17), suggesting exchange is limited to formation of $\text{CsPb}(\text{NO}_3)_3$ and $\text{CsPb}(\text{BF}_4)_3$ rich layers at the NP periphery. Interestingly, if NO_3^- is added in a slow incremental manner, a significant increase in UV absorption < 380 nm is observed that is not observed for BF_4^- (Fig. S18-S19). We postulated the new feature is likely due to oxidation of I^- to I_3^- by excess NO_3^- , and subsequently constructed a simple optical assay for oxidants in non-polar media. Figure 8c shows a photograph of CsPbBr_3 and CsPbI_3 PL response when exposed to different concentrations of NO_3^- and ClO_4^- in hexane. The NO_3^- immediately quenches the PL from CsPbI_3 but not of CsPbBr_3 , while ClO_4^- quenches both at the higher concentrations. The quenching of the P-NP PL was expected based on comparison of the two electron standard reduction potentials (E^0) of NO_3^- and ClO_4^- with the oxidation potentials of I^- to I_3^- and Br^- to Br_2 (Fig. S20).³² Taking the ion size and reduction potential into account, we considered that converting CsPbBr_3 to $\text{CsPbBr}_{1-x}\text{F}_x$ would result in highly stable P-NPs. To this end, successive additions of tetraoctylammonium chloride (TOACl) and excess tetrabutylammonium fluoride (TBAF) to a solution of $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ NPs lead to a broad absorbance spectra below 350 nm (Fig. S21), which is congruent with recent calculations of the band gap in cubic CsPbF_3 (3.8 eV).³³ Direct titration of unpurified CsPbCl_3 with F^- could also be reversed with the addition of TOACl, suggesting that CsPbF_3 can be prepared in the future.

Taken together, these results suggest a multitude of future spectrochemical uses of P-NPs. For example, phase transfer catalysts are important for a wide variety of organic reactions, especially those in non-polar conditions where traditional catalysts have low solubility.³⁴ The added functionality of a colorimetric response over the course of a reaction may open new paradigms in monitoring chemical kinetics. Here we focused on a simple organohalide transformation, but future nanoparticle designs may allow for monitoring of, or reacting with, a

number of reactive leaving groups during synthesis. Finally, the ability to colorimetrically detect ions at low concentrations by eye using this approach may lead to novel bench top assays being developed,^{35,26,36} or sensing at the single molecule level may be achieved by harnessing the high quantum yields of the perovskite nanoparticles.

CONCLUSION

The halide exchange between CsPbX_3 ($\text{X} = \text{Cl}^-$, Br^- , I^-) perovskite nanoparticles and tetraoctylammonium halide salts (TOAX) were studied by absorption and fluorescence measurements to calibrate colorimetric response to halide type and concentration. Using this as a foundation, the CsPbX_3 were used as halide reservoirs in Finkelstein like exchange reactions involving organohalides. It was demonstrated that CsPbI_3 could be used as an I^- source for the exchange from 2-bromododecanoic acid to 2-iodidodecanoic acid in non-polar media. The complementary exchange of Br^- to CsPbBr_3 resulted in colorimetric change, which provided a means to follow reaction kinetics in real time. Finkelstein exchange, and the role of ligands in the reaction were further monitored by NMR. Combined with the TOAX studies that provided precise halide calibrations, reaction kinetics were then quantified as a function of 2-bromododecanoic acid and perovskite nanoparticle concentration, which revealed first order kinetics for the halide reservoir, confirming Finkelstein exchange. Finally, the use of CsPbX_3 nanoparticles to colorimetrically assay ions in solution was demonstrated, with colorimetric response being quantitatively related to halide type and concentration, as well as free anions in solution, which led to either color change or PL quenching due to oxidation of halide in the lattices.

METHODS

Synthesis of CsPbX₃ (X = Cl⁻, Br⁻, I⁻) Perovskite Nanoparticles (P-NPs). The synthesis of cesium lead halide nanoparticles was achieved following a previous procedure reported by Kovalenko.¹⁶ Briefly, 0.8 grams of cesium carbonate was dissolved in 30 mL of octadecene (0.16 M solution) along with 2.5 mL of oleic acid and heated at 120 °C under vacuum for 1 h. Similarly, stock solutions of oleylamine (OAm) and oleic acid (OAc) were vacuum dried at 120°C for 1 h. All solutions were put under Ar and stored in a glove box until needed. Next, 0.188 mmol of PbX₂ (0.052g PbCl₂, 0.069 g of PbBr₂, 0.084 g of PbI₂ for CsPbCl₃, CsPbBr₃, and CsPbI₃, respectively) and 5 mL of octadecene (ODE) were combined and the mixture was vacuumed at 120 °C for 1 h. After drying, the mixture was put under Ar and 0.5 mL of oleic acid and 0.5 ml of oleylamine were injected with vigorous stirring. After the PbX₂ had completely dissolved, the temperature was raised to 140 °C and 0.4 mL (0.06 mmol) of the cesium oleate mixture was injected. The solution turned turbid with high luminescence under UV excitation (except for CsPbCl₃ where no PL was observed) and was immediately cooled in ice water. Particles were diluted in hexane and cleaned *via* 1-Butanol (1-BuOH) precipitation on demand prior to use.

Halide Exchange with alkylammonium halide salts. In a typical experiment, an aliquot of the diluted stock solution in hexane of P-NPs (324 µg/mL) was added to an Eppendorf tube and µL increments of a stock 13 mM tetraoctylammonium halide (TOAX) in 1-BuOH was slowly added to achieve the desired concentration. Mixed solvent systems were done identically but after diluting P-NPs with 1-BuOH. Concentrated solutions in hexane required 30-60 s for complete reaction after stirring.

Finkelstein Exchange Reactions. Stock solutions of 13 mM 2-bromododecanoic acid [2-Br] and octylamine (OA) in hexane were prepared. In this study, [2-Br]:[OA] = 1 unless otherwise noted. In a typical reaction, a solution of CsPbX₃ NPs (~15 µg/mL) in hexane was prepared to which

the desired amount of amine was added first, followed by the desired amount of 2-Br. The reaction was either carried out in a sealed round bottom flask or sealed cuvette under N₂ gas, or in a open glass 96-well plate.

Anion Assays: Non-halide alkylammonium salts were prepared (see SI) and diluted to 0.1M stock solutions. Spectral data was acquired using solutions of 54 µg/mL of the cleaned P-NPs. The oxidizer well plate experiment utilized 100 µL of a 65 µg/mL P-NP solution for each of the four wells of CsPbI₃ and CsPbBr₃, with the first well serving as the control. Next different amounts of alkylammonium nitrate or cesium perchlorate were added to the wells, mixed with a glass pipette, and allowed to react for ~10 s. Samples were imaged under UV irradiation.

Associated Content

Supporting Information including experimental procedures, Figures S1-S22, and a movie of solvent gradient based ion exchange in CsPbI₃ P-NPs. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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