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Detection of Halomethanes Using Cesium Lead Halide Perovskite Nanocrystals

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 ABSTRACT: The extensive use of halomethanes (CH₃X, X = F, Cl. Br. L) as refrigerants, propellants, and preticides has drawn
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Cl, Br, I) as refrigerants, propellants, and pesticides has drawn serious concern due to their adverse biological and atmospheric impact. However, there are currently no portable rapid and accurate monitoring systems for their detection. This work introduces an approach for the selective and sensitive detection of halomethanes using photoluminescence spectral shifts in cesium lead halide perovskite nanocrystals. Focusing on iodomethane (CH₃I) as a model system, it is shown that cesium lead bromide (CsPbBr₃) nanocrystals can undergo rapid (<5 s) halide exchange, but only after exposure to oleylamine to induce nucleophilic substitution of the CH₃I and release the iodide species. The extent of the halide exchange is directly



dependent on the CH_3I concentration, with the photoluminescence emission of the $CsPbBr_3$ nanocrystals exhibiting a redshift of more than 150 nm upon the addition of 10 ppmv of CH_3I . This represents the widest detection range and the highest sensitivity to the detection of halomethanes using a low-cost and portable approach reported to date. Furthermore, inherent selectivity for halomethanes compared to other organohalide analogues is achieved through the dramatic differences in their alkylation reactivity.

KEYWORDS: halomethanes, iodomethane, perovskite nanocrystals, photoluminescence, sensor

he high reactivity of iodomethane (methyl iodide, CH₃I) confers both its potential utility and hazard in human applications. Since its approval for use as a pesticide by the United States Environmental Protection Agency in 2007, it has gained popularity as a fumigant for insect and fungus control.^{1,2} However, there has also been strong academic scrutiny and public concern regarding its latent toxicity^{3,4} due to the possible mutagenic and carcinogenic effects arising from its strong reactivity with biological nucleophiles after prolonged exposure.⁵ In support of this, the Occupational Safety and Health Administration (OSHA) has established that an 8 h time-weighted average limit for CH₃I of 2 ppm is considered safe to avoid irritation and liver or kidney damage. Furthermore, CH₃I can release its constituent iodine atoms via photodecomposition, which can subsequently react with atmospheric ozone to produce the monoxide radical, IO, leading to ozone-depletion in the troposphere and stratosphere.^{6,7} An accurate on-site method for monitoring CH₃I has remained elusive because of this high reactivity, together with the difficulty of detection due to its odorless and colorless nature.

Traditionally, CH_3I detection relies on sophisticated instrumentation, such as gas chromatography coupled with mass spectrometry (GC-MS) or flame ionization detector (GC-FID) based methods.^{7–10} However, these techniques are restricted to the laboratory environment and require complex sample preparation. An alternative approach involves the use of more affordable and portable spectroscopic methods. For example, a limit of detection (LOD) for CH_3I of 5.3 ppt was achieved using resonance fluorescence detection of atomic iodine (170–190 nm),⁶ although the utility of this system is greatly reduced by its low selectivity. The strong alkylating ability of CH_3I (iodide as a leaving group) compared with other organoiodide analogues has been exploited to meet the

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Figure 1. Reaction mechanisms and spectroscopic response of CsPbBr₃ perovskite nanocrystals (PNCs) to CH₃I. (a) Oleylamine (OLA, 0.96 mM) or CH₃I (20 000 ppbv solution) were introduced separately into PNC dispersions in toluene. The emission images under 365 nm UV light were recorded after 100 min, showing no change in emission. (b) OLA pretreated CH₃I solutions (CH₃I concentration: 20 000 ppbv) were added to a PNC dispersion in toluene, with the emission color under 365 nm UV light before and 20 s after addition. The hypothesized reaction mechanism, where CH₃I induces the alkylation of OLA by an S_N2 mechanism and stops at dimethyl analogue formation. (c) UV– visible absorption spectra of PNCs exposed to varying amounts of CH₃I. (d) Emission spectra of CsPbBr₃ PNCs as a function of the amount of added CH₃I.(Inset: redshift of PNC PL emission as a function of CH₃I concentration. Linear fitting of results from 100 to 10 000 ppbv shown as a red line with $R^2 = 0.997$). (e) CIE chart converted from the PL spectra of PNCs exposed to varying amounts of CH₃I. (Note: Spectra in c, d, were recorded 20 s after CH₃I addition at room temperature to ensure the reaction was complete).

selectivity requirements. After alkylation, organic or organometallic luminescent probes, such as cyclometalated iridium-(III) complexes¹¹ and pyridine-based π -conjugated oligomers/ polymers, ^{1,5,12,13} change their optical properties indirectly in response to the methyl functional group in CH₃I. However, those indirect mechanisms proceed over minutes to hours, leading to low sensitivity (>100 ppb) and long measurement time. Therefore, it is critical to develop a reliable method for more rapid, selective, and sensitive detection of CH₃I.

For this purpose, we focus on highly photoluminescent inorganic cesium lead bromide $(CsPbBr_3)$ perovskite nanocrystal (PNC) dispersions that are designed to efficiently interact with CH₃I. The photoluminescence (PL) characteristics of PNCs are known to be highly dependent on the nature

of the halide anion in the crystal lattice.¹⁴ For the model system investigated here, the bromide derivative supports facile ion exchange with a PL signal in the visible wavelength range. Furthermore, their highly ionic nature enables their optoelectronic properties to be readily engineered through facile and rapid (an)ion exchange.¹⁵ Through such exchange processes, tunable emission wavelengths throughout the entire visible spectrum (390–780 nm) with near-unity PL quantum efficiency (PLQE) can be achieved.¹⁶ This tunability is typically exploited for optoelectronic applications,¹⁷ although preliminary work has shown this phenomenon to be useful for the detection of hydrochloric acid, with an LOD of 5 ppm.¹⁸

Here, we utilize the ability of such PNCs to undergo rapid halide exchange as a signal transduction method to detect



Figure 2. Changes to the morphology and crystal structure of CsPbBr₃ PNCs exposed to varying amounts of CH₃I. (a) TEM images of pristine PNCs, showing a cuboid shape. (b, c) TEM images of PNCs after reaction with 1000 and 3000 ppbv solutions of CH₃I. (d) TEM images of PNCs on addition of 6000 ppbv CH₃I showing almost complete loss of the cuboid PNCs, with the remaining phase comprising 2DRP nanosheets. (e) XRD patterns of PNCs exposed to various CH₃I amounts, which showed a standard CsPbBr₃ cuboid signal at both 15.2° (100) and 30.6° (200) for the pristine sample.

CH₃I. Subsequent halide exchange of the bromide in the PNCs with iodide results in a rapid bathochromic shift in the PL emission spectrum. Time-dependent spectroscopic measurements reveal that these PL changes are accompanied by a complex structural transformation of the nanocrystals. It is also shown that the detection of CH₃I using CsPbBr₃ PNCs requires a sacrificial nucleophile (Nu:) to initially react with CH₃I and release the iodide. Moreover, the large differences in the rate of nucleophilic substitution reaction between various organoiodines $(R_3C:I)$ and the nucleophile provide a high degree of selectivity of the PNC-based indicator for CH₃I. First-principles density functional theory (DFT) calculations further confirm that the chemical interactions between the resulting oleylammonium iodide and the PNC surface are stronger than for CH₃I, providing a thermodynamic basis for the high sensitivity of the indicator. This serves as a representative system for the detection of halomethanes using cesium halide PNCs more generally.

RESULTS AND DISCUSSION

Activating CH₃I for Halide Exchange. Direct exposure of CsPbBr₃ PNCs in toluene to CH₃I solutions did not cause any discernible change in PL properties over modest time scales (Figure 1a and Figure S1a). This demonstrates that efficient halide exchange in perovskites occurs only between ionic halide species and not with covalently bound iodine species.²⁰ To activate the sensor system, in this work, oleylamine (OLA, $C_{18}H_{35}NH_2$) was a convenient choice of nucleophile given its use in the synthesis of the CsPbBr₃ PNCs:

$$R_3C:I + R'N:H_2 \rightarrow [R_3C:NH_2R']^+ + I:^-$$
(1)

An S_N^2 reaction between CH_3I and an excess of OLA (R'-NH₂) initially yields *N*-methyl oleylammonium iodide (eq 1), whereas further reaction with additional OLA yields *N*-methyl oleylamine and an oleylammonium iodide salt, as illustrated in Figure 1b.^{19,21} A subsequent alkylation reaction with CH_3I is also possible, resulting in the formation of N,N-dimethyl oleylamine and additional oleylammonium iodide. Evidence supporting this reaction mechanism was obtained with a model OLA analogue, dodecylamine, using NMR and GC-MS measurements (Figures S2 and S3, see the Supporting Information for additional details).

The use of OLA in the synthesis of PNCs in the present work results in the concomitant formation of its protonated ammonium form when an acid is also present in the reaction medium, such as oleic acid.²² The OLA and/or oleylammonium salts subsequently passivate the surface of the nanocrystals.²³ The addition of excess OLA into the PNC dispersions did not cause any changes in their PL emission wavelength (Figure 1a and Figure S1b). In contrast, when a toluene solution of CH₃I and OLA (CH₃I:OLA = 1:3 molar ratio) was added to a dispersion of the PNCs, significant changes in the optical properties of the PNCs were observed (Figure 1b-d). The red-shift in the UV-visible absorption and PL emission spectra upon CH₃I addition is the result of a decrease in the optical bandgap of the cuboid nanocrystals, which is direct evidence for the exchange of bromide with iodide in the lattice of the CsPbBr₃ PNCs.²⁴ Notably, the dramatic redshift in PL is linearly correlated with the CH₃I concentration in the range of 100 ppbv to 10,000 ppbv (Figure 1d), and is sufficiently large to provide a practical visual response according to the CIE chart shown in Figure 1e.

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Figure 3. Integrated steady-state photoluminescence and millisecond time-dependent emission spectra. (a) Integrated steady-state PL intensity difference displayed as a function of $CH_{3}I$ concentration for the three different stages of the reaction: stage A ($CH_{3}I \le 100$ ppbv), stage B (100 ppbv < $CH_{3}I \le 3000$ ppbv), and stage C ($CH_{3}I > 3000$ ppbv). (b–d) Time-dependent emission spectra of $CsPbBr_{3}$ PNCs at $CH_{3}I$ concentrations of 100, 1000, and 6000 ppbv, respectively. The PNC emission images under 365 nm UV light at 5 and 20 s, and the schemes of structural transformation are shown in the lower panels of b–d. It is found that the OLA-reacted $CH_{3}I$ in Stage A ($CH_{3}I \le 100$ ppbv) acts as a trap passivator, whereas at higher $CH_{3}I$ concentrations, it causes the PNCs to undergo (i) surface disruption/PNC decomposition, (ii) iodide migration, and (iii) surface passivation processes in stages B and C. (Note: PL emission signals stabilized after 20 s.)

Further inspection of the absorption spectra for samples with CH_3I concentrations above 3000 ppbv show an increased absorption at shorter wavelengths, which suggests the possible concurrent formation of 2D Ruddlesden–Popper perovskite (2DRP) nanosheets.²⁵ The generalized chemical formula for

2DRP nanosheets is given by $L_2[ABX_3]_{n-1}BX_4$, where A is a monovalent inorganic or organic cation, such as cesium (Cs⁺), methylammonium (MA⁺), or formamidinium (FA⁺), B is a divalent metal ion (usually Pb²⁺ or Sn²⁺), and X is a halide anion. L represents a monovalent organic cation that is usually



Figure 4. Radiative relaxation dynamics as measured by time-resolved photoluminescence (TRPL) measurements, and response studies at different CsPbBr₃ concentrations and temperatures. (a) Quantitative values of slow, fast, and average PL decay as calculated from the biexponential fitting of the time-resolved PL decays of CsPbBr₃ PNCs before and after addition of various concentrations of CH₃I, and the corresponding PL redshifts. Schematic of the radiative dynamic processes in (b) an ideal PNC without vacancies, where the photon is absorbed and radiatively recombined, and (c) a PNC with vacancy defects, which generate shallow states that cause trapping of the carriers and a slowing of their recombination dynamics. (d) Simulated PL redshifts (lines) of PNCs as a function of CH₃I concentration, with the colored symbols corresponding to experimental data. (e, f) Time-dependent PL emission spectra of the sensor system at 15, 25, and 35 °C at a CH₃I concentration of 1000 and 6000 ppby, respectively. (g) Relative PL redshift at 15, 25, and 35 °C after adding CH₃I at a concentration of 1000 or 6000 ppby, with average fluctuations $\leq 3.5\%$ and $\leq 3.4\%$, respectively, after 20 s.

larger than A^+ and the value of *n* is the number of metal halide layers. The UV-visible absorption energy profile (Figure 1c) and other results discussed below are consistent with the 2DRP nanosheets having n = 1 and n = 2.²⁶

Evolution of Structural and Spectroscopic Properties. To correlate these spectroscopic changes with the underlying structural transformations in the PNCs, we conducted transmission electron microscopy (TEM) and X-ray scattering measurements. TEM images of the as-synthesized PNCs reveal a well-defined cuboid morphology, with an average size of about 11 nm (Figure 2a and Figure S4a). For CH_3I concentrations up to 3000 ppbv, high-resolution TEM



Figure 5. (a) Change in the photoluminescence peak energy of the PNCs as a function of the total introduced halide species (CH₃I or other iodine containing species) relative to the starting bromide concentration within the PNC sensor solution. The dotted gray trendline is derived from literature values of the energy difference at various ratios of CsPbI₃:CsPbBr₃.²⁴ Reproduced with permission from ref 24. Copyright 2015 American Chemical Society. (b) PL redshifts of PNCs with OLA-treated equimolar organoiodine analytes in IPA at various concentrations. Iodoethane, iodopentane, iodohexane, and iodotoluene impart no change to the emission color of CsPbBr₃PNCs due to the lack of iodide formation. Meanwhile, other alkyl ammonium iodide salts reacted less efficiently than OLA-treated CH₃I. (c, d) Schematic representation and histogram of the surface interaction energies of OLAI, MAI or CH₃I onto the native CsPbBr₃ surface. The atomistic representations are obtained after a complete relaxation of the slab models with CsBr-terminated surface using first-principles density functional theory (DFT) methods.

(HRTEM) images indicate the progressive expansion of the (100) lattice spacing in the cuboid CsPbBr₃ PNCs from 5.9 to 6.4 Å due to iodide substitution (Figure 2a–c). Although the cuboid geometry is retained at low CH₃I concentrations, clear evidence for the dissolution of the cuboid phase of the PNCs and the concurrent formation of 2DRP nanosheets is seen at higher CH₃I concentrations (Figure 2c, d). Laterally stacked 2DRP assemblies are observed upon addition of 3000 ppbv CH₃I (Figure 2c), with the interlayer spacing of 10.0 Å correlating well with that of nanosheets.²⁶

X-ray diffraction (XRD) measurements confirm that perovskite nanocuboids exist (Figure 2e), although discrimination between the cubic and orthorhombic phases requires a more detailed structural analysis.²⁷ A progressive shift of the nanocuboid XRD peaks toward lower 2θ values occurs with increasing concentrations of CH₃I, in accordance with the expected lattice expansion within the iodide-rich PNCs. Moreover, consistent with HRTEM, the XRD results also indicate the formation of 2DRP at CH₃I concentrations of 3000 ppbv and higher.^{28,29} The partial transformation from 3D perovskites into 2DRP nanosheets is further supported by comparing the 2D grazing incidence wide-angle X-ray scattering (GIWAXS) measurements of the samples containing 1000 and 6000 ppbv CH_3I (Figure S4b, c).^{30,31}

The structural transformation of the CsPbBr₃ PNCs involves a complicated halide exchange process. It has been suggested that this occurs through a reaction-limited exchange at the surface of the PNCs, with subsequent fast ionic diffusion occurring within the nanocrystal lattice.³² The spectroscopic properties of the PNCs reflect this complexity. The changes in the PL emission color occur gradually and over multiple stages of halide exchange as a function of CH₃I concentration (Figure 3). These stages can be categorized first according to their relative PL intensity changes (Figure 3a), with a slight enhancement of the emission (stage A) followed by a rapid decrease (stage B) and then a gradual transition toward nearly complete quenching (stage C) being observed. Further inspection of the temporal changes in the UV-visible absorption and PL emission within these stages reveals vastly different dynamics (Figure S5). UV-visible absorption

properties are retained in stage A (Figure S5a, b), whereas the PL emission exhibits a slight redshift and enhanced intensity (ca. 10%) after an induction period of a few seconds (Figure 3b). This behavior is indicative of a surface passivation effect.^{33,34} During stage B, the UV–visible absorption spectrum intensity of the PNCs remains unchanged (Figure S5c, d), whereas the PL emission initially vanishes and then partly recovers at a red-shifted wavelength (Figure 3c). Finally, in stage C the cuboid PNCs undergo rapid dissolution and renucleation as 2DRP nanosheets (Figure S5e, f), thus resulting in a largely suppressed PL emission (Figure 3d).

For completeness, to understand the role of excess OLA across these stages, we conducted control experiments using equivalent OLA additions but without any CH_3I (Figure 3a). Only a slight PL emission intensity enhancement, with no change in the peak position (see Figure S1b), was observed at the higher OLA concentrations. This demonstrates that the spectroscopic changes across the three identified stages are directly related to the alkyl ammonium iodide species generated in solution and not to the residual OLA. A schematic depiction of the structural transformation across these stages is presented in Figure 3b-d.

Sensing Parameters. To further correlate the ensuing structural and spectroscopic properties, we studied the radiative relaxation dynamics of the PNCs using time-resolved photoluminescence (TRPL) measurements. The PL excitation spectra in Figure S6a suggest that, in both stage B and stage C, energy transfer occurs from small n-value 2DRP nanosheets to nanocuboids, consistent with previous reports.^{35,36} The absence of PL from the 2DRP phases suggests that this energy transfer results in efficient quenching of PL from the 2DRP phases, and for this reason, the PL from the nanocuboids only is considered here. Analysis of the TRPL decay curves using an empirical biexponential function yields average PL lifetimes that show a gradual increase with increasing CH₃I concentrations (Table S1). This is consistent with the fact that iodidebased cuboid PNCs exhibit longer radiative lifetimes than their bromide analogues (Figure 4a).^{37,38} An accelerated slow decay in stage A suggests a reduction in the number of shallow states due to trap filling.^{39,40} Meanwhile, the progressive increase in the lifetime of this component and its overall magnitude across stages B and C are indicative of more defective cuboid PNCs being generated (Figure 4b, c). This confirms that the structural transformation across these stages yields lowerquality cuboid PNCs.

The chemical and structural transformations across these three stages are evidently dependent on the interaction between the oleylammonium iodide species in solution and the perovskite nanocrystals. To explore this dependence, the changes in the PL redshift as a function of the PNC concentration are plotted in Figure 4d. The results can be readily described by a semiempirical formalism that considers the concentration of PNCs (denoted as [PNC]) as a fitting parameter (see the description of PL Response Modeling in SI). Collectively, the results show that tuning the [PNC] provides a facile way to modulate the sensitivity window for CH₃I detection, with lower concentrations yielding higher sensitivity factors. Given that the practical range for [PNC] is \sim 1 nM to \sim 1 mM, the achievable linear sensitivity window for detection of CH₃I, through [PNC] modifications alone, is ~10 ppbv to $\sim 10\,000$ ppmv.

To gauge the practical limit of the thermal response window for this sensor system, we measured the PL emission characteristics between 5 and 45 °C for 1000 and 6000 ppbv CH₃I concentrations as representative samples (Figure 4e–g and Figure S8). It was found that the response time is slightly longer at lower temperatures for the lower CH₃I concentration sample, whereas temperature had little effect on response time at the higher CH₃I concentration. Apart from slight differences in initial reaction dynamics, after a 20 s stabilization period, the PL redshifts are consistent to within $\pm 3.5\%$ at temperatures between 15 and 35 °C (Figure 4g). This provides a practical temperature range for the reliable operation of a sensor platform based on this approach.

Reaction Mechanisms. The selectivity of the PNCs for the CH₃I system was measured using a range of organoiodine compounds including iodomethane, iodoethane, iodopentane, iodohexane, iodotoluene, methyammonium iodide (MAI), formamidinium iodide (FAI), n-butylammonium iodide (n-BAI), and tetrabutylammonium iodide (TBAI) after pretreating with OLA (see Figure 5a, b). Negligible changes to the PL emission peak wavelength were observed for all tested organoiodines, apart from CH₃I. This demonstrates the high degree of selectivity for CH₃I, which can be understood by considering the dramatic differences in reaction rates of different organoiodines toward nucleophilic substitution. For a typical S_N2 reaction involving haloalkanes, the reaction rate (R), given by $R = k[Nu:][R_3C:X]$, is dependent on the rate constant (k), the concentrations of the nucleophile (i.e., OLA in our case) and the specific organoiodine compound. Among the organoiodine derivatives studied here, CH_3I has a k value that is more than 30 times larger than the others (Figure S10).^{19,21} This facilitates much faster overall dynamics, which leads to inherent selectivity for CH₃I in the CsPbBr₃ PNC system (Figure S11). Furthermore, this finding validates the need to generate halide salts to induce the rapid transformation of the PNCs into halide exchange analogues.

Importantly, the chemical nature of the alkyl ammonium halide salt also impacts the extent of the exchange process. This is evident from the substantially smaller spectral changes (Figure 5a, b and Figure S12a) and the slower exchange dynamics (Figure S12b, c) observed for the various ammonium iodide salts compared to those for an equivalent concentration of CH₃I reacted with OLA. When the PL peak changes are compared to the ratio of the total iodide added vs the parent bromide concentration (as determined from the [PNC]), a universal curve is found for the individual iodide species (Figure 5a). This confirms that (i) the transformation mechanism in these systems is primarily dependent on the ratio of added iodide/parent bromide; (ii) the different iodine sources have varied PL change characteristics; and (iii) the OLA-activated CH₃I provides the greatest sensitivity across the tested iodine sources evaluated in the present work.

To provide further thermodynamic insights into these transformation trends, we explored the interaction energies between CH₃I, OLAI, and MAI with the PNC surface using first-principles density functional theory (DFT) calculations (Table S2 and Figure 5c, d). The predicted positive surface interaction energy ($\Delta E_{\rm SI}$) between CH₃I and PNCs reveals a thermodynamically unfavorable chemical interaction. On the other hand, taking MAI and OLAI as representatives, the large negative surface interaction energies demonstrate that these alkyl ammonium salts favorably interact with the PNC surface. We further investigated these potential chemical reaction pathways (Table S2 and Figure S13). The reaction enthalpy of pure I/Br exchange ($\Delta E_{\rm re3}$) is much lower than that of just Cs

substitution by alkyl ammonium (ΔE_{re1}) for both MAI and OLAI, indicating that halide exchange could occur spontaneously prior to other processes on the native surface of CsPbBr₃. Nonetheless, this advantage diminishes when 25% pre-existing surface passivation with OLA is taken into account. It can be seen that OLA⁺ substitution becomes the rate-limiting step for halide migration in passivated PNCs (Figure S13), which is also consistent with the above-mentioned spectroscopic effects in Figure 3. On the whole, the larger negative reaction energies of OLA⁺ compared to the shorter alkyl ammoniums, such as MA⁺ (ΔE_{re1} and ΔE_{re2} , see Table S2), contribute to more efficient surface disruption, in turn enabling more extensive halide migration within the PNCs.

CONCLUSIONS

In summary, we have extended the versatility of cesium lead halide perovskite to the detection of widely used halomethanes, enabling their application as rapid, selective, and sensitive chemical sensors. The transduction mechanism involves an efficient alkylation reaction between the halomethane and a nucleophile. In the present work, the liberated iodide anions undergo exchange with bromide anions in the perovskite lattice, which in turn leads to structural reconfiguration of the CsPbBr₃ PNCs. The ensuing changes in the PL properties of the PNCs provide a linear spectroscopic response and enable quantitative detection of CH₃I between 100 ppbv to 10 000 ppbv, with a limit of detection of 30 ± 10 ppbv and a response time of 5 s at room temperature. The detection sensitivity and range could be appropriately adjusted by tuning the PNC concentration in the reaction system. Furthermore, the significant differences in the alkylation rate of nucleophiles by halomethanes compared with other organohalides enable excellent selectivity to be achieved. This facile transduction mechanism provides a platform for the development of an onsite luminescence-based sensor system suitable for both visual and instrumental readout.

METHODS AND EXPERIMENTAL

Materials and Chemicals. Lead(II) bromide (PbBr₂, 99.999% trace metals basis), cesium carbonate (Cs₂CO₃, 99.995% trace metals basis), oleylamine (OLA, technical grade, 70%), diisooctylphosphinic acid (DPA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%), iodomethane (CH₃I, 99.5%, copper as stabilizer), iodoethane (CH₃CH₂I, 99%, copper as stabilizer), iodoethane (CH₃CH₂I, 98%, copper as stabilizer), 1-iodohexane (\geq 98%), 2-iodotoluene (98%), *n*-butylammonium iodide (n-BAI, 98%), and tetrabutylammonium iodide (TBAI, \geq 99.0%) were from Sigma-Aldrich. Toluene (99.5%) and isopropanol (IPA, 99.5%) were from Merck. Methylammonium iodide (MAI, 99%), and formamidinium iodide (FAI, 99%) were from Dyenamo. All chemicals were used without further purification.

Preparation of Cs-DPA. Cs_2CO_3 (100 mg, 0.31 mmol) was added to a 25 mL two-neck flask containing ODE (5 mL) and DPA (0.5 mL) at room temperature. After that, the mixture was degassed and heated at 120 °C under a vacuum (ca. 2 mbar) for 30 min to remove residual oxygen and water. The flask was refilled with N₂ gas with the temperature subsequently raised to 150 °C. The temperature was maintained until the complete dissolution of Cs_2CO_3 , as evidenced by the mixture becoming transparent. The solution was stored under N₂ at room temperature, and was heated to 120 °C prior to injection in the subsequent reactions.

Synthesis of CsPbBr₃PNCs. PbBr₂ (69 mg, 0.188 mmol) was added to ODE (5 mL) in a 50 mL three-neck flask, with OLA (0.5 mL) and DPA (0.5 mL) then added to the suspension at room

temperature. The mixture was then degassed and heated to 120 °C under vacuum (ca. 2 mbar) with stirring for 30 min in order to remove residual oxygen and water in the solution and dissolve the PbBr₂ salt. The milky solution became transparent upon dissolution of the PbBr₂. The flask was then filled with N₂ gas, and the temperature was raised to 160 °C. The preheated Cs-DPA solution (0.4 mL) was then injected swiftly into the reaction solution. Immediately after injection, the solution was quickly cooled to room temperature in an ice bath. The resulting crude PNC solution was then stored under ambient conditions.

Isolation and Purification of CsPbBr₃ PNCs. The crude reaction solution was mixed with pure IPA (crude solution: IPA = 1:3 v/v) first in an ambient environment. The mixture was then centrifuged at 10 000 rpm for 5 min. The supernatant was discarded after centrifugation. The precipitated CsPbBr₃ PNCs were then redispersed in pure toluene to give a solution that was colloidally stable over an extended period.

Preparation of PNC Sensor and Analyte Solutions. The perovskite NC sensor solution was prepared by diluting the washed perovskite dispersion spectra with toluene to 3 mL. The concentration of PNCs in the sensor solution was adjusted and maintained at about 9.32 \pm 0.15 nM, which was calculated by the absorption and the relative molar extinction coefficient as determined in the study of Maes et al.⁴¹ A stock solution of CH₃I was prepared by adding CH₃I (10 μ L, ~30.9 μ M) into pure toluene (1 mL), followed by the addition of OLA (ca. 90 μ M). This solution was then diluted 120-fold and a portion was added to the sensor solutions were prepared using a similar method except changing pure toluene to pure IPA.

Characterization. Samples for powder X-ray diffraction (XRD) were prepared by drop-casting a PNC dispersion onto a glass substrate, which was then dried without heating in an ambient environment. XRD patterns were collected by a Bruker D8 Advance diffractometer equipped with a Cu-K α radiation source operated at 40 kV and 40 mA, and equipped with a high-speed line-position sensitive Lynxeye XE detector. Transmission electron microscopy (TEM) images of each sample on ultrathin carbon grids were collected using a Tecnai G² T20 TWIN (FEI Company) microscope equipped with a LaB₆ electron emitter. The steady-state absorption and emission spectra were recorded with a commercial spectrometer (StellarNet) equipped with a CCD camera (Silver-Nova-TEC-X2), using a halogen lamp (SL1) or 390 nm excitation source (SL1-LED), respectively. The relative time-course experiment spectra were collected using the same system. Time-resolved photoluminescence (TRPL) spectra were measured using an FLS 980 spectrometer (Edinburgh Instruments) with a 405 nm pulsed diode laser for excitation with a 500 kHz frequency (average power up to 6.25 μ W) and the maximal emission wavelength of each sample used for detection. The 2D grazing incidence wide-angle X-ray scattering (GIWAXS) was measured at the SAXS/WAXS beamline at the Australian Synchrotron.^{42,43} The energy of the incident X-ray beam was fixed at 15 keV. The 2D scattering patterns were acquired using a Dectris Pilatus 1 M detector with an exposure time of 1 s and an incident angle of 0.2°. GC-mass spectra were obtained with a Thermo Scientific TSQ 8000 TRACE 1310 GC mass spectrometer using electron ionization in the positive ion mode with ionization energy of 70 eV. Gas chromatography was performed on a SGE SOLGEL-1MS column (30 m \times 0.25 mm ID, 0.25 μm film thickness), with a temperature program of 50 °C for 2 min, then heating at 25 °C/min to 300 $^\circ\text{C},$ where the temperature was held for 8 min with a split injection, split ratio of 10, an injector temperature of 300 °C and the transfer line was set to 300 °C. High-purity helium was used as carrier gas with a flow rate of 1 mL/min. ¹H NMR measurements were performed on a Bruker Bio Spin Av400H with a 9.4 T magnet and a 5 mm inverse 1H-X BBI autotuning broadband probe at a ¹H frequency of 400.13 MHz in toluene- d_8 .

Computational Methods. First-principles density functional theory (DFT) calculations were carried out using the Vienna ab Initio Simulation Package (VASP).⁴⁴ The projector augmented wave (PAW)⁴⁵ pseudopotentials were utilized to describe core and valence

electrons, and the generalized gradient approximation based on the Perdew–Burke–Ernzerhof (GGA-PBE)⁴⁶ form was selected to describe electron exchange and correlation. Grimme's energy correction method was employed to correctly account for the dispersion interactions.⁴⁷ Various chemical reactions at the CsBrterminated neutral surface of CsPbBr₃ nanocrystals were investigated using a slab model consisting of a 2 × 2 surface unit cell and eight layers of the CsPbBr₃ crystal. For calculating the reaction enthalpies, all models were fully relaxed to account for the lattice expansion due to Cs substitution and I/Br exchange. In all cases, plane wave kinetic energy cutoff was set to 450 eV.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c08794.

Synthesis of CsPbI₃; ¹H NMR and GC-MS; PL response modeling; TRPL fitting table; time-dependent absorption spectra, size distribution, and temperature-dependent PL/UV-visible absorption of CsPbBr₃ under various CH₃I concentrations; selectivity/efficiency optical analysis; and the additional detection of various bromide sources by CsPbI₃ PNCs (PDF)

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[†]W.Y. and H.L. contributed equally to this work. W.Y. and J.J.J. conceived and designed the experiments, under the technical support from P.M. and W.W.H.W; W.Y., H.L., and B.T. performed the experiments; W.Y., H.L, and J.J.J. analyzed and constructed the results. W.H. and C.R.M. performed the GIWAXS measurement. A.D.S. performed the time-resolved photoluminescence experiments: A.S.R.C. helped with the GC-MS and NMR measurements and analysis. M.W. and N.M. performed first-principles DFT calculations. W.Y., A.S.R.C., and J.J.J. mainly worked on the manuscript, with all the authors contributing to the drafting and correction.

Notes

The authors declare no competing financial interest.

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