

## Article

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# Colloidal Nanocrystals as a Platform for Rapid Screening of Charge **Trap Passivating Molecules for Metal Halide Perovskite Thin Films**

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**ABSTRACT:** Charge recombination at surface trap sites is a significant impediment to metal halide perovskite (MHP) thin film-based optoelectronic devices. To passivate the surface charge traps, chemical treatments with molecules that bind to the MHP thin film surfaces can be employed. However, the current approaches to test the trap passivation efficacy of molecules on thin film surface suffer from limited through-put and low statistical significance. Here, we demonstrate the use of colloidal MHP nanocrystals (NCs) as an experimental platform for high-throughput screening of charge trap passivating molecules for MHP thin films. Using CsPbX<sub>3</sub> (X = Br, I) NCs, over 20 molecules were rapidly screened for their surface trap passivation efficacy. Our approach identified tri-*n*-butylphosphine (TBPh) as a superb charge trap passivating molecule on MHP surfaces. TBPh treatment brings the photoluminescence quantum yield of CsPbBr<sub>3</sub> NCs to near unity and also results in superior surface trap passivation of MHP thin films, even when compared to a previously reported treatment with pyridine. Our work highlights the benefits of utilizing the high surface area-to-volume ratio of NCs for the accelerated study of surface trap passivation using molecular treatment and then translating the findings to bulk semiconductors. This approach is broadly applicable to a wide range of semiconductors as long as they can be synthesized into NCs.

Over the past decade, metal halide perovskites (MHPs) have generated a tremendous amount of interest due to their high performance in a wide array of optoelectronic devices such as solar cells,<sup>1-8</sup> light-emitting diodes (LEDS),<sup>9-13</sup> photodetectors,<sup>14-17</sup> lasing,<sup>18-20</sup> and sensors.<sup>21</sup> In particular, MHP solar cells have achieved power conversion efficiencies (PCE) approaching 23%,<sup>22</sup> which is on-par with the silicon solar cells and the highest among all low-cost solution processable materials. The high device performance of MHPs stems from a combination of their favorable properties such as a high light absorption coefficient, long charge carrier diffusion lengths,<sup>23-26</sup> and long carrier lifetimes.<sup>27-32</sup>

However, despite the progress so far, there are still major challenges to be overcome for MHP devices. 13, 17, 33-35 A particularly important issue is understanding and controlling the charge recombination in MHPs. Recently, Yang et al.<sup>28</sup> demonstrated that charge recombination on the top and bottom surfaces of the polycrystalline thin films typically employed in devices is orders of magnitude higher than the bulk recombination. Additionally, there have been numerous studies examining the impact of the external environment (e.g. inert atmosphere, ambient conditions, high oxygen conditions, under vacuum, etc.)<sup>7, 36-40</sup> on charge recombination at the surface of these materials. These studies highlight the importance of controlling charge trapping at surface defects in order to achieve improved device performance.<sup>28, 35, 41-44</sup>

To passivate the surface charge trap sites, various approaches have been investigated such as treatment with organic molecules,<sup>29,41,44-53</sup> polymers,<sup>54-56</sup> and inorganic materials such as Al<sub>2</sub>O<sub>3.<sup>57-59</sup></sub> Pyridine<sup>30, 32, 60, 61</sup> has been the most commonly employed organic molecule for surface ACS Paragon Plus Environment

trap passivation on MHP thin films while other molecules containing amine/ammonium,<sup>44, 49, 52, 62-66</sup> phosphonic acids,<sup>53,67</sup> and sulfur-containing head groups including thiols, thiophene, and/or thiocyanate<sup>32, 41, 47, 50, 54, 68</sup> have been employed as well. However, most of the previous reports have been limited in the number of molecules per study. Challenges associated with overcoming low signals from surface states versus bulk states, while also employing a large enough sample size to build statistical significance, have limited the number of molecules that can be used in systematic and controlled comparison experiments with thin films. These obstacles have impeded the identification of optimal trap passivating molecules and rendered a more complete understanding of the relationship between surface chemistry and charge trap sites elusive.

Here we demonstrate colloidal nanocrystals (NCs) as an experimental platform for high-throughput screening of surface trap passivation molecules for semiconductor thin films. Utilizing NCs as a model system for thin films surfaces can help overcome the previously stated challenges in thin films studies. One advantage is that optical properties of NCs are strongly influenced by surface states, alleviating the surface versus bulk signal issues. For example, a NC with a 5-nm diameter can have nearly half of its

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atoms on the surface, amplifying the surface charge recombination effects versus the bulk. Moreover, colloidal NC solutions are compatible with solution-based optical and chemical characterization methods that produce data with high signal-to-noise ratios.<sup>69, 70</sup> Additionally, a single synthesis batch of NCs can produce gram-scale quantities with only a few milligrams required per test with colloidal solution. This allows for a single batch of NCs to provide dozens of individual surface passivation tests on identical samples, facilitating consistency in comparative studies with a large variety of test molecules.<sup>71</sup> In this study, we exploited these attributes to perform a systematic and comparative study of various candidate molecules for surface trap passivation on MHP NCs and tested the validity of translating the NC screening results to thin film samples. As a model system, we employed  $CsPbX_3$  (X = Br, I) NCs to rapidly screen 23 molecules with various head groups. Our approach identified tri-n-butylphosphine (TBPh) as a trap passivating molecule that exhibited higher efficacy when compared to previously reported molecules, such as pyridine. TBPh was found to increase the photoluminescence quantum yield (PLQY) of NCs to near unity. Applying a TBPh treatment to various MHP thin film compositions resulted in superior PL intensity and lifetime improvements compared to untreated control and equimolar pyridine-treated films. Finally, the TBPh treatment was applied to MHP solar cell devices and resulted in increased open-circuit voltage ( $V_{0C}$ ), fill factor (FF), and PCE.

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CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs were synthesized *via* the hot-injection method developed by Protesecu *et al.*<sup>72</sup> (see Methods section for details). The two halide compositions were examined in order to probe any possible halide-dependent responses to the surface treatments.<sup>73-76</sup> The assynthesized NCs were characterized with absorbance spectroscopy, PL spectroscopy, and high-resolution transmission electron microscopy (HR-TEM) (Figure 1). For the purposes of this work, the NCs with edge lengths averaging 10 nm were prepared such that they have minimal quantum confinement effects and therefore an electronic structure closer to their bulk crystal counterparts.<sup>72</sup> As seen in Figure 1A and B, both CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs are cubic shaped with relatively narrow size dispersions of 8% and 10%, respectively.

The purification of the NCs was modified to avoid the use of excess oleylamine (OLAM) and oleic acid (OA) and provide the barest possible surface of the NCs (see purification method 1 in Methods section for details). The relatively more exposed surfaces increase the sensitivity to the ligand treatment tests. This point will be further elaborated on later. PLQY was employed to monitor the non-radiative charge trapping in the NCs and was measured as a function of concentration of the various test ligand molecules in solution. The starting PLQYs for the as-synthesized CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs were 58% and 29% respectively. It should be noted that these PLQY values are lower than previously reported values<sup>63, 67, 68, 72, 73, 77-79</sup> but should be expected due to the intentional modification of the purification process in which excess OLAM and OA were not added. To check for any dependence of results on initial NC surface quality and PLOY, we also prepared another set of CsPbBr<sub>3</sub> NCs with a



**Figure 1.** Characterization of the as-synthesized CsPbX<sub>3</sub> NC using high-resolution transmission electron microscopy (TEM) for (a) CsPbBr<sub>3</sub> and (b) CsPbI<sub>3</sub> NCs as well as (c) NC absorption and photoluminescence spectra.

more common method of adding OLAM and OA during purification (see purification method 2 in Methods section), which resulted in initial NC PLQY of 73%, consistent with the previously reported PLQY values<sup>63, 67, 68, 72, 73, 77-81</sup>.

The candidate molecules for surface trap passivation were added to solutions of the as-synthesized NCs and the PLQY was subsequently measured. The ligand exchange is expected to occur quickly based on the law of mass action and the dynamic equilibrium between free and bound ligands on NC surfaces.82 Moreover, De Roo et al.77 revealed that the ligand-surface interactions in MHP NCs are even more dynamic compared to metal chalcogenide NC systems such as PbSe or CdSe. In order to better understand the PLQY results, one must consider a multitude of factors starting with the notion that the added ligand molecules can either bind directly to the surface or undergo ligand exchange reactions with the natively bound ligands (OLAM and OA in our model system<sup>72,77</sup>). The binding motif of the ligand molecules can be understood through the covalent bond classification developed by M. L. H. Green.<sup>83, 84</sup> In particular, the native oleylammonium (OLAM<sup>+</sup>) and oleate (OA<sup>-</sup> ) ligands are thought to bind to the surface of the NCs as a pair of X-type ligands.77 Therefore, other ligand species that can undergo proton exchange reactions to form charged head groups, such as carboxylic acids, amines, or thiols, can be involved in X-type ligand exchange reactions with the

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**Figure 2.** Photoluminescence quantum yield (PLQY) results of (a) CsPbBr<sub>3</sub> and (b) CsPbI<sub>3</sub> NCs, which have a mixture of oleic acid (OA) and oleylamine (OLAM) as the native ligands, in response to ligand additions. The PLQY of the as-synthesized NCs are indicated as the dotted lines. The (\*) is placed next to samples that showed increased PLQY upon initial scans but did not show NC stability lasting beyond 1 hour in solution. The overall error of the relative PLQY method is ±3%.

native ligands. Further, it is possible that L-type ligands (Lewis bases such as phosphines, pyridine, thiophene, or amines) may undergo a ligand exchange reaction with natively bound L-type ligands.<sup>77, 82, 83</sup> Electron pair accepting

Z-type ligands, such as lead (II) oleate (Pb(oleate)<sub>2</sub>), can exchange with other native Z-type ligands. Lastly, L-type and Z-type ligands can bind with each other through a Lewis



**Figure 3.** PL intensity and lifetime for (a-b) CsPbBrI<sub>2</sub> and (c-d) CsPbI<sub>3</sub> thin films comparing untreated films to TBPhand pyridine-treated films. The CsPbBrI<sub>2</sub> films exhibited almost three orders of magnitude increase in PL intensity with the TBPh treatments as well as an increase in lifetime, indicating increased surface passivation.

acid-base reaction, which can lead to the removal of both species from the NC surface.<sup>82</sup>

In this work, all three binding motifs outlined above were utilized to probe their relative efficacy of surface passivation of MHP NCs. Carboxylic acid/amine combinations, which form carboxylate and ammonium ions, were used as X-type ligands<sup>77</sup>, as they have been previously demonstrated to act as such together, and chain length was varied to elucidate potential trends in steric effects. It would be expected that these X-type pairs would interact with both the surface bound Pb or Cs atoms while the interaction with the Pb atoms is expected to play a more significant role in the photoluminescent properties due to the construction of the band edges<sup>85</sup> and that shorter chains would have the potential to allow for greater surface coverage. Pb(oleate)<sub>2</sub> was tested as a Z-type ligand, which is expected to bind with surface halide sites. Furthermore, several Lewis base L-type ligands were used in this work — including amines, pyridine, thiols, thiophene, sulfoxides, and phosphines — to investigate the effects of different head

groups versus trap passivation efficacy. These molecules are expected to interact with surface Pb or Cs atoms as they are electron-donating molecules. This study was focused on studying organic ligand molecules even though there has been some recent progress in encapsulating perovskite NCs in inorganic materials.<sup>80, 81, 86</sup> Also, it should be noted that the results can be somewhat convoluted with the potential removal of the native ligands through various exchange reactions with the test molecules. Nonetheless, it should be reiterated that we apply the purification modifications to deliberately reduce the number of native ligands on the NC surface and diminish the potential complications with ligand exchange mechanisms.

Figure 2 summarizes the results of the various ligand additions and can generally be categorized into two main outcomes – an increase or decrease in NC PLQY with respect to the additions. A reduction in PLQY can occur if the added test molecules go through ligand exchange reactions with the native ligand molecules and (1) are less effective in surface trap passivation compared to the native

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**Figure 4.** PL intensity and lifetime scans for (a-b) CsPbBrI<sub>2</sub> and (c-d) CsPbI<sub>3</sub> thin films comparing the control films to the sulfolane-treated surfaces. Both film compositions exhibit reduced PL intensity and lifetime upon treatment with sulfolane. The lifetimes for the CsPbI<sub>3</sub> scans were taken at the respective PL peak positions.

ligands, (2) are unable to stay strongly bound to the NC surface, and/or (3) too strongly ligate NC components to the point of NC digestion. The latter is the likely outcome from the addition of most of the sulfoxides, after which the NC solution turned colorless. This is consistent with previous reports that showed sulfoxides having strong interactions with Pb<sup>2+</sup> ions and typically being used to help solubilize precursors.<sup>1,4,87,88</sup>

In contrast, addition of molecules such as TBPh and OA resulted in increased PLQY of both CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs, indicating improved trap passivation to the assynthesized NC surface. It should be noted that a positive correlation between PLQY and the ligand addition conclusively identifies the test molecules as effective trap passivation species for the following reason. A positive correlation necessarily means that either the test molecules bind to available open surface sites without significantly removing the native ligands, thus providing additional trap passivation, or they replace the native ligands and provide more effective charge trap passivation than the native ligands. In either case, with the observation of increase in PLQY, one can unambiguously identify molecules that provide good surface passivation. Therefore, the rapid, high-throughput and statistically significant screening of molecules with NCs can easily identify promising test molecules for thin film samples and devices.

Among the test molecules that resulted in increased PLOY compared to the as-synthesized NCs, several factors were considered when selecting the most promising molecule for the thin films surface trap passivation. First, the molecules that resulted in poor NC stability (marked by star symbols in Figure 2) or lowered PLQY at higher concentrations were excluded. The reduction in PLOY at higher concentrations occurs with most of the amine species, the carboxylic acid/amine combinations, and sulfoxides. Some of these results are due to dissolution of NCs at high enough concentration of ligands that bind too strongly to either perovskite components, the likely case with the sulfoxides.<sup>1,4,87,</sup> <sup>88</sup> and in agreement with previous reports of excess OA and OLAM in the NC solutions causing the dissolution of the NCs.<sup>72, 73, 77</sup> These molecules that digest NCs are not ideal for subsequent use on thin films in this study as they will likely result in significant dissolution and/or morphological changes in thin films. Dissolution of the thin films is

undoubtedly not desired for their characterization and device fabrication, and significant morphological changes will make it difficult to distinguish whether any response to the exposure to the test molecules is due to trap passivation by the molecules or structural changes of the grains. Second, some molecules such as Pb(oleate)<sub>2</sub> showed a peak at certain ligand concentrations (initial increase at low concentrations but reduction at higher concentrations) without dissolution of NCs, which may be function of ligand-exchange reaction equilibria between the new ligands and native ligands at the NC surface. At lower concentrations, it 10 may be possible for the new ligands to bind to NC surface 11 without significantly removing the native ligands, thus re-12 sulting in improved PLQY. At higher concentrations, the 13 new ligands may bind to a large fraction of the native lig-14 ands, resulting in their removal from the NC surface. If the 15 new ligands do not provide as sufficient of trap passivation 16 as the native ligands, it will result in lowered PLQY. For the 17 purpose of this study, with the focus being the first demonstration of achieving improved surface passivation in thin 18 films with newly identified ligand molecules from the rapid 19 NC screening, these molecules were not pursued. Third, 20 some molecules exhibited significant differences in surface 21 passivation of CsPbBr3 and CsPbI3 NCs. For example, thio-22 phene, pyridine, and dodecanethiol (DDT) appear to im-23 prove the PLQY of the CsPbI<sub>3</sub> NCs, which is agreement with 24 previous thin film reports,<sup>30, 32, 41, 50</sup> but the same molecules 25 decrease the PLQY of the CsPbBr<sub>3</sub> NCs. These results reveal 26 that the different halides result in significant differences in 27 surface chemistry and the nature of traps. This is not sur-28 prising since the different halides would cause significant 29 differences in electronic structure of the band and surface trap sites. Indeed, previous reports that showed the varying 30 degrees of complexation strength<sup>89</sup> and overall stability 31 based on halide composition.<sup>90-92</sup> The elucidation of the ex-32 act binding motif and surface-ligand exchange mechanisms 33 with different molecules and NC compositions will be highly 34 valuable. However, that is beyond the scope of this study, 35 which is focused on the first demonstration of NCs as a 36 probe for rapid identification of molecules for surface trap 37 passivation in thin films. Therefore, in this study, we focus 38 on identifying the most promising molecule for a test study 39 to see if the NC results get successfully translated to thin 40 films. Further studies with a larger scope on the NC surface 41 chemistry are currently being pursued in our laboratory. 42

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43 Ultimately, our screening approach identified tributylphosphine (TBPh) to be a promising surface trap 44 passivation molecule for translation to thin films. The addi-45 tion of TBPh resulted in improved PLQY for both CsPbBr<sub>3</sub> 46 and CsPbI<sub>3</sub> compositions while also exhibiting a positive 47 correlation between concentration and PLQY with reten-48 tion of NC stability. In particular, for CsPbBr<sub>3</sub>, the PLQY rose 49 to 100%, within an error bar of 3%, upon addition of TBPh. 50 This improved trap passivation was verified to be inde-51 pendent of NC purification method as the similar results 52 were obtained from NCs prepared with a more common pu-53 rification method (see purification method 2 in Methods 54 section). TBPh treatment increased the PLQY of these NCs 55 from 73% to 100%, within the uncertainty of the measure-56 ment, as well (Figure S1). These results suggest that TBPh 57 provides a complete surface trap passivation for CsPbBr<sub>3</sub> 58

NCs either on its own or in combination with native OLAM\* and OA<sup>-</sup> ligands. It is most likely that TBPh is acting as an Ltype ligand and donating a lone pair to a metal ion. While this is only one possible mechanism whereby TBPh could be binding to the surface, it is not yet known if it is in a ligand exchange reaction or a cooperative binding motif. The elucidation of the complex nature of the TBPh binding therefore requires detailed spectroscopic investigations. This is beyond the scope of this work and is being pursued in our laboratory. Additionally, the TBPh treatment did not alter the structural integrity of the NCs in the concentration range used in this study to achieve the high PLQY result, as can be seen in TEM images in Figure S2. For CsPbI<sub>3</sub>, the addition of TBPh resulted in one of the larger increases in PLQY but only up to 40%. This suggests that, in contrast to CsPbBr<sub>3</sub> case, a combination of TBPh, OLAM<sup>+</sup> and OA<sup>-</sup> ligands are not able to passivate all of surface trap sites on CsPbI<sub>3</sub> NCs, or provide proper changes in the electronic structure for complete trap removal. Despite the varying degree with CsPbBr3 and CsPbI3, the increased PLQY for both upon TBPh addition suggests that TBPh is a promising candidate molecule for thin films studies.

After the NC testing identified TBPh as among the most promising trap passivation molecules, three compositions (CsPbBr<sub>3</sub>, CsPbI<sub>3</sub>, and CsPbBrI<sub>2</sub>) of MHP thin films were treated with TBPh to test its trap passivation efficacy on polycrystalline thin films. The CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> compositions were chosen so as to mirror the NC testing. The mixed halide CsPbBrI2 was selected due to its increased phase stability over pure CsPbI<sub>3</sub> and capability to form pinhole free thin films for device fabrication with promising solar cell performance.<sup>93-96</sup> The CsPbBr<sub>3</sub> thin films were not able to be made sufficiently pin-hole free for use in solar cell devices (Figure S3). For a direct comparison of the charge trap passivation efficacy of TBPh with previously reported molecules, it was compared to an equimolar pyridine treatment, which has been the most commonly used molecule in the literature.<sup>30, 32, 60, 61</sup> To treat the films, the TBPh or pyridine ligands were suspended in toluene, a non-polar solvent that would not induce significant reconstruction of MHP surface, and statically dispensed on the MHP films before being spun off (see Methods section for details). SEM images (Figure S4) show that samples that were treated with TBPh or pyridine solution in toluene with up to 0.26 mM concentrations do not result in any appreciable morphological changes in MHP thin films.

Upon treatment with TBPh, the MHP thin films exhibited significant increases in PL intensity (Figures 3A and C and Figure S5A for CsPbBr<sub>3</sub>), up to three orders of magnitude for the CsPbBrI<sub>2</sub> composition. The TBPh treatments resulted in larger increase in PL intensity as compared to the equimolar treatment with pyridine which mirrors the results from NC screening that identified TBPh to be superior to pyridine in reducing non-radiative recombination at the surface. In addition to testing molecules that increased PLOY of NCs, sulfolane treatment was investigated to examine how species that decreased NC PLQY affect the thin films. As shown in Figure 4 and Figure S5B, the sulfolane treatments decreased the PL intensity of all CsPbBrI<sub>2</sub>, CsPbI<sub>3</sub> and CsPbBr<sub>3</sub> thin films. For CsPbI<sub>3</sub> film, the sulfolane

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**Figure 5.** Results from  $CsPbBrI_2$  thin film solar cell devices. (a) J-V curves of an untreated and a 0.26 mM TBPh-treated device, as well as statistics demonstrating the improvement in (b) device PCE, (c)  $V_{oc}$ , and (d) FF over the untreated devices.

treatment led to a red-shift in the PL peak position, indicating that there could be grain/surface reconstruction. Nonetheless, these results show that the influence of the chemical treatment on MHP thin films mirror the NC PLQY results also for molecules that result in decreased surface trap passivation.

The PL lifetime measurements also show consistent results. TBPh treated CsPbBrI<sub>2</sub> and CsPbI<sub>3</sub> samples exhibit slower carrier recombination compared to their respective control as well as pyridine-treated films (Figure 3B, D and Figure S6), while the sulfolane treated films (Figure 4B and D) exhibit faster carrier recombination versus the untreated control films. The average lifetimes (Table S1) for the CsPbBrI<sub>2</sub> films increased from 18 ns up to 75 ns with the TBPh treatments. Since surface recombination has been shown to have major effect on carrier lifetime,<sup>28, 30-32</sup> these results provide further evidence of the NC PLQY results being translated to the thin film systems well. These mirroring results of the NC and thin film samples demonstrate that, while there may be some differences in how charge carriers behave in the two systems,<sup>97, 98</sup> the NC system is an adequate platform for rapid screening of surface passivating molecules for thin films.

In order to study the impact of various ligand treatments on solar cell performance, CsPbBrI<sub>2</sub> based devices (ITO/TiO<sub>2</sub>/CsPbBrI<sub>2</sub>/Spiro-MeOTAD/Au) were fabricated and tested. All perovskite thin film deposition, ligand treatment, and subsequent device fabrication and testing steps were performed inside N2 filled gloveboxes (see Experimental Section for details) to avoid any complications from exposure to ambient air that may affect surface passivation.<sup>36-38</sup> To this end, Co(III)-doped Spiro-MeOTAD was used as the hole transporting layer in order to avoid the oxidation step in the ambient air required by the more typically used lithium-doped Spiro-MeOTAD.61, 99-101 Figure 5 shows the results of the device testing for the TBPh-treated surface with statistics from 36 devices per condition. The TBPh treatment enhances the overall PCE of the devices, and in particular the Voc and FF parameters show the largest response. Voc improvements have been linked to a reduction in surface recombination through various mechanisms involving shallow and deep trap site alleviation<sup>30, 98,</sup> <sup>102-104</sup> and reducing ion migration at the surfaces.<sup>43, 105, 106</sup>



**Figure 6.** The relationship between PLQY of the CsPbBr<sub>3</sub> NCs with the 9.0mM ligand treatments versus the  $V_{oc}$  of the thin film devices treated with the same ligands (sulfolane, pyridine, "as-synthesized"/controls, and TBPh from left to right).

These types of mechanisms can lead to a charge carrier accumulation at the surface/interface which leads to increased charge recombination and/or the development of an additional electric field that can hinder charge extraction.<sup>43</sup> While the direct interaction mechanism of the TBPh is not yet known, it is expected to act as a Lewis base L-type ligand, meaning its interactions with surface-bound Pb atoms would be the most likely mechanism of surface passivation.<sup>32, 82, 83, 107</sup> Under-coordinated Pb atoms can result in electron trap sites<sup>108</sup> which can cause electron accumulation at the perovskite/HTL interface, but the TBPh passivation would reduce the electron trap sites leading to the improved V<sub>0C</sub> and charge extraction.<sup>29, 42, 44, 48, 61, 102</sup>

Similar to the NC testing and thin film results, the TBPh treatments resulted in superior device performance compared to equimolar pyridine treatment (Figure S7). Treatment with sulfolane resulted in reduced Voc and PCE of solar cells (Figure S7), which is also consistent with the NC screening results. Figure 6 shows a relationship between the NC PLQY and the  $V_{oc}$  of the thin film devices when treated with different ligand molecules. It should be noted that making any direct correlation across different ligand molecule treatments is complicated by the differences in surface-ligand and ligand-ligand interactions as well as differences depending on perovskite compositions (see Figure S8 for CsPbI<sub>3</sub> NC PLQY results). However, the positive relationship between the NC PLOY and the V<sub>oc</sub> of the thin film devices observed for both CsPbBr<sub>3</sub> NCs (Figure 6) and CsPbI<sub>3</sub> NCs (Figure S8) supports the notion that employing NCs for rapid identification of molecules that can successfully passivate thin film surfaces is a good starting point.

In conclusion, our report demonstrates colloidal NCs as high-throughput screening platforms for rapid identification of surface charge trap passivating molecules for semiconductor thin films. By utilizing this approach, we screened more than 20 molecules using CsPbX<sub>3</sub> NCs as model systems and identified tri-*n*-butylphosphine (TBPh) to be a highly effective surface trap passivation molecule for CsPbX<sub>3</sub> MHP thin films and solar cell devices. The approach demonstrated in this work may be broadly applied to a wide range of semiconductor materials as long as they can be synthesized into NCs, but further studies are required to verify the generality. Having the capability to systematically study a large array of molecules with the identical samples and experimental controls will reveal important trends that would have been difficult to reliably obtain with bulk or thin film studies. This can lead to accelerated progress towards a deeper understanding of charge trap sites on semiconductor surfaces.

#### Methods

#### Materials:

All materials were purchased from Sigma Aldrich unless otherwise specified.

#### Preparation of Cesium Oleate Solution

A stock solution of cesium oleate in octadecene (ODE) was prepared a procedure similar to Protesescu *et al.*<sup>72</sup> Cs<sub>2</sub>CO<sub>3</sub> (0.407 g) was loaded into a 50mL 3-neck flask along with 20mL ODE and 1.25 mL of oleic acid (HOA). The solution was dried under vacuum for 1 hour at 120°C and then heated under argon at 150°C for 30 minutes. Solution was stored in an N<sub>2</sub> glovebox for long-term storage. Solution was heated to 100°C prior to use in CsPbX<sub>3</sub> NC synthesis.

#### CsPbX<sub>3</sub> NC Synthesis

CsPbX<sub>3</sub> NCs were prepared following previously reported procedures.<sup>72</sup> PbX<sub>2</sub> (0.75 mmol), such as (0.276 g PbBr<sub>2</sub> [Alfa Aesar 99.999%] or 0.347g PbI<sub>2</sub> [TCI 99.999%]), were loaded into a 100 mL 3-neck flask along with 20 mL ODE, 2 mL OA, and 2 mL oleylamine (OLAM) and then dried under vacuum at 110°C for 1 hour. The solution was then placed under an Argon and then heated to the injection temperature (180°C for CsPbBr<sub>3</sub> and 150°C for CsPbI<sub>3</sub>) before 0.8 mL of warmed cesium oleate were swiftly injected. The solution was placed into an ice bath 5-10 seconds after the injection. After the reaction solution was cooled it was placed in an Argon atmosphere storage flask *via* cannula transfer and brought into the N<sub>2</sub> atmosphere glovebox for purification.

#### CsPbX<sub>3</sub> NC Purification

Method 1: The pure reaction solution was centrifuged at 6000 rpm for 40 minutes. The lightly colored supernant was discarded and the solids were dispersed in 5 mL of toluene [anhydrous]. The new solution was centrifuged at 3000 rpm for 3 minutes to remove large aggregates and the supernant was saved. The purified solution was stored in the  $N_2$  glovebox for long-term storage.

Method 2: A method similar to ref. 77 was used, but methyl acetate (MeOAc) was used in place of acetone<sup>77</sup>. A 1:1

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volume ratio of MeOAc to reaction solution was centrifuged at 6000 rpm for 20 minutes. The supernant was discarded and the solids were dispersed in 5 mL of toluene [anhydrous]. 4 vol.% dried HOA and 4 vol% dried OLAM were added to the solution and agitated. 5 mL of MeOAc was then added to the solution and was centrifuged at 6000 rpm for 20 minutes. The supernant was discarded and the solids were again dispersed in 5 mL of toluene. 1.5 vol.% dried HOA and 1.5 vol.% dried OLAM were then added to the solution. 5 mL of MeOAc was added to the solution and was again centrifuged at 6000 rpm for 20 minutes. The supernant was again discarded and 5 mL of toluene was added to the remaining solids. The solution was centrifuged at 3000 rpm for 3 minutes to removes excessively large solids and supernant was saved. The purified solution was stored in the N<sub>2</sub> glovebox for long-term storage.

#### Ligand Additions

Materials used for ligand species were either anhydrous or dried using a "freeze, pump, thaw" method and brought into the N<sub>2</sub> glovebox. Species used were: acetic acid (AceticA), octanoic acid (OctA), oleic acid (OA), propylamine (PropAM), butylamine (ButAM), tributylamine (TriButAM), octylamine (OctAM), olyelamine (OLAM), sulfolane, dimethyl sulfoxide (DMSO), butyl sulfoxide (BSO), phenyl vinyl sulfoxide (PVSO), 1-tetrahydrothiophene oxide (THTO), tetrahydrothiophene (THT), thiophene, pyridine, tri-*n*-butyl phosphine (TBPh), dodecane thiol (DDT), and trioctylphosphine (TOPh).

Lead oleate (Pb(oleate)<sub>2</sub>) was synthesized by adding 1M PbO and 2M HOA to ODE. The solution was then heated to  $120^{\circ}$ C under vacuum for 1 hour. The solution was placed under Argon and transferred to a storage flask also under Argon for transfer and storage in the N<sub>2</sub> glovebox. The solution was warmed to  $50^{\circ}$ C prior to usage since it was a solid at room temperature.

#### CsPbX₃ Thin Films

CsPbX<sub>3</sub> films were produced following previous reports.<sup>94-96</sup> 0.43 M solutions consisting of 0.224 g CsI [Alfa Aesar 99.999%] and appropriate ratios of PbBr<sub>2</sub> and PbI<sub>2</sub>, based on desired final halide composition, were placed in 2 mL dimethylformamide (DMF) [anhydrous] and stirred at 60°C for 1 hour to fully dissolve components. The solution was then passed through a 0.2  $\mu$ m PTFE syringe filter and into a storage vial. Care was taken to make sure solution did not crystallize on the threads or sides of the vial. Thin films were prepared by dynamically dispensing 45  $\mu$ L of the filtered precursor solution at 1,500 rpm for 50 seconds. The resulting film was then annealed for 10 minutes at either 345°C for the CsPbBrI<sub>2</sub> films and 350°C for the CsPbI<sub>3</sub> films.

The CsPbBr<sub>3</sub> solutions replaced the DMF with dimethyl sulfoxide (DMSO) [anhydrous]. Additionally, the solution was dynamically dispensed at 1,500 rpm for 60 seconds and 200  $\mu$ L of chlorobenzene was dropped on the film 45 seconds into spinning in order to increase surface coverage. The resulting films were then annealed at 330°C for 10 minutes.

#### CsPbBrI<sub>2</sub> Solar Cell Devices

Pre-patterned ITO substrates were cleaned via sonication using a Hellmanex soap solution for 5 minutes, followed by sonication in DI H<sub>2</sub>O and then ethanol. The clean substrates were then UV-ozone treated for 5 minutes. Compact titanium dioxide (c-TiO<sub>2</sub>) electrodes were prepared by spin casting a solution of 146 µL Ti(iPO)<sub>2</sub>(acac)<sub>2</sub> in 2 mL butanol [anhydrous] at 4,000 rpm for 60 seconds. The films were then annealed at 500°C for 5 minutes and transferred to the nitrogen glovebox after cooling. The perovskite films were cast in the same method described above. Once the films had cooled, the top film surface was treated. For the control samples, 300 µL of toluene was placed on the film and allowed to sit for 60 seconds before spinning off at 3,000 rpm. For the treated films, the 300 µL of toluene was replaced by a solution containing the specified ligand concentration in toluene and allowed to sit for 60 seconds before spinning off at 3,000 rpm as well. Subsequently, 45 µL of Spiro-MeTAD solution (72 mg Spiro-MeTAD [Lumtec], 17.5 µL of 1.8M Li:TFSI in acetonitrile [anhydrous], 29.0 µL of 0.2M FK209 [Lumtec] in acetonitrile, and 28.8 µL of tBP in 1.0 mL of chlorobenzene [anhvdrous]) was dynamically dispensed at 4.000 rpm for 30 seconds and then dried at 60°C for 10 minutes. The devices were then finished with 50 nm Ag electrodes. The fabricated solar cells were then tested under N<sub>2</sub> atmosphere to keep them completely isolated from oxygen and moisture.

#### **Optical Characterization**

Photoluminescence (PL) spectra were collected on a PTI Quantamaster 400 (QM-400) system. For thin film samples, the perovskite films were kept from air exposure using a glass slide and UV-cured epoxy to seal the edges. Absorbance spectra were collected using a PerkinElmer Lambda 950S spectrophotometer. For photoluminescence quantum yield (PLQY) measurements were collected using the relative PLQY method, which was first verified using Rhodamine 6G and Rhodamine 101, and then appropriate standard fluorescent dyes were used for NP measurements. Fluorescent lifetimes were measured using time correlated single photon counting (TCSPC) setup on the QM-400 system using a 633 nm laser diode. Average lifetimes were obtained by fitting decay curves with a biexponential function and then using the integrated area under the curve representing each function to calculate a weighted average.

#### Electron Microscopy

High-resolution transmission electron microscopy (TEM) images were taken using a FEI Titan 80-300 TEM using 300 kV accelerating voltage. All images were taken at room temperature and care was taken to prepare TEM grinds in such a way that minimized air exposure. Scanning electron microscopy (SEM) images were taken on a Quanta 650 SEM operating at 5 kV. All samples were imaged in multiple locations to confirm homogeneity of samples and images shown are representative of center areas of prepared films.

Solar Cell Testing

The devices were tested using a Keithley source-meter using a scan rate of 1 V/s under AM 1.5 illumination from a solar simulator (PV Measurements). The light source was calibrated using a reference silicon solar cell (PV Measurements). The device area was 0.03 cm<sup>2</sup>. An optical mask was used to block illumination to the non-device area during testing.

#### ASSOCIATED CONTENT

Supporting Information available: Additional PL and lifetime data, SEM images, and device statistics are provided. This information is available free of charge at http://pubs.acs.org.

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#### Conflict of Interest

The authors declare no competing financial interest.

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