

Communication

Lead-Halide Perovskites for Photocatalytic #-Alkylation of Aldehydes

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Lead-Halide Perovskites for Photocatalytic α-Alkylation of Aldehydes

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Supporting Information Placeholder

ABSTRACT: Cost-effective and efficient photocatalysis are highly desirable in chemical synthesis. Here we demonstrate that readily prepared suspensions of APbBr₃ (A = Cs or methylammonium (MA)) type perovskite colloids (*ca.* 2-100 nm) can selectively photocatalyze carbon-carbon bond formation reactions, *i.e.* α -alkylations. Specifically, we demonstrate α alkylation of aldehydes with a turnover number (TON) of over 52,000 under visible light illumination. Hybrid organic/inorganic perovskites are revolutionizing photovoltaic research and are now impacting other research fields, but their exploration in organic synthesis is rare. Our low-cost, easy-to-process, highly-efficient and bandedge-tunable perovskite photocatalyst is expected to bring new insights in chemical synthesis.

Carbon-carbon (C-C) bond formation is one of the most fundamental transformations in organic synthesis. Nature is capable of storing solar energy in chemical bonds via photosynthesis. The photoconversion process, involves a series of C-C bond forming photoredox catalytic reactions starting from CO2 and light.^{1,2} Tremendous advances in artificial photoredox C-C bond formations have been made, including the development of robust and reliable protocols to merge photoredox catalysis with organocatalysis.3-5 Å fundamental aim is the development of new modes of small molecule activation via cheap, effective and easyto-process catalytic systems. Many protocols, including Ru/Irbased complexes,³⁻⁶ organic dyes,⁷ semiconductors QDs ^{8,9} etc., can be employed under mild reaction conditions and have broad substrate scope. However, typically these systems either need noble metals or require complicated synthetic protocols, both of which are not desirable.

The recent renaissance in ABX₃ hybrid perovskite semiconductors has revolutionized photovoltaics, enabling solution-processable solar cells that have now reached 23.3% power conversion efficiency.¹⁰⁻¹³ In addition to the exceptional photovoltaic performance, hybrid perovskite systems have also demonstrated breakthroughs in piezoelectrics,¹⁴ high-gain photodetectors,¹⁵
light-emitting diodes,¹⁶ lasers ¹⁷ and transistors.¹⁸ The excellent photovoltaic and optoelectronic performance is attributed to beneficial opto-electronic properties, such as, strong light absorption,¹⁹ long charge-carrier lifetimes^{20,21} and long charge-carrier diffusion lengths.^{22,23} Our previous work also reported low trap densities and small surface recombination velocities, leading to a noticeable enhancement of the photo-generated carrier lifetime and mobility.^{19,24,25} Thus, given the beneficial properties

for photovoltaic applications, they also should be of interest in photocatalytic applications.^{26,27}

Here we report a cost-effective, highly-efficient and easy-toprocess photocatalytic system centering on ABX₃ Pb-halide perovskite nanocrystals (NCs) for direct C-C bond formation reactions. To demonstrate their photocatalytic characteristics, we explore a model reaction, α -alkylation of aldehydes, a widely employed valuable chemical transformation. Particularly, we demonstrate that APbBr₃ NCs can directly photocatalyze the α alkylation reaction with high yield and without N₂-sparging. By slight modification of the reaction conditions, we show that our photocatalytic system can selectively catalyze other important chemical reactions, such as, sp³ C-couplings and alkyl-halide reductions. The perovskite photocatalyst studied here are a versatile material system easily prepared from earth-abundant elements and low-cost starting materials.¹⁰ The as-prepared NCs are not only stable in common organic solvents (Fig. S1-5), but also are effective in photocatalysis with a TON of over 52,000 for α -alkylation, three orders of magnitude higher than precious Ir or Ru catalysts. As a result, the perovskite photocatalyst are much more economical than Ir/Ru (2-order cost lower, Table S1), rendering them as new promising candidates for broad application in organic synthesis.

The exploration of the perovskites' photocatalytic characteristics for organic synthesis was inspired by a simple one-pot reaction (Fig. 1a). After mixing of the readily available starting materials in an open vial, a one-pot perovskite emissive suspension was formed due to the solvents' emulsion/de-emulsion effect.²⁸ To the resulting suspension organic substrates 2-bromoacetophenone **1a**, and octanal **2a** are added at room temperature. Upon blue-LED illumination, several products are generated, including dehalogenated acetophenone **3a** (yield 76%), sp³ C-coupling product **4a** (8%), and α-alkylation product **5a** (7%). Next, we explore the photocatalytic selectivity towards the desired product.

Gram scale colloids of APbBr₃ are readily prepared and are further isolated via centrifugation. We obtained perovskite colloids with sizes ranging from 2 ~100 nm (Fig. 1b and S2). Perovskites' photoluminescence (PL) is shown in a variety of solvents (Fig. 1c and S3a). The PL lifetimes in various solvents are recorded from ~10 to ~100 ns which are long-lived enough to induce charge transfer in these catalytic systems according to Nicewize.⁸ (Fig. 1d and S3b) The lifetimes do not exhibit single exponential decay times likely resulting from a broad size distribution.²⁸ Overall, these NCs' are significantly larger than the reported Bohr radius of APbBr₃, and thus their optical properties

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resemble that of their thin film versions.^{29,30} The colloids display a major absorption peak at 500 nm and PL at 513 nm in hexane, indicating a band gap energy of 2.4 eV matching well with bulk APbBr₃. X-ray diffraction (Fig. 1e) confirmed the perovskite structure.^{10,11}



Figure 1. (a) The one-pot reaction demonstration; (b) TEM of CsPbBr₃; (c) Absorption and PL spectra of CsPbBr₃ in different solvents. Inset: under ambient light (left) and 365 nm UV light (right); (d) PL lifetimes of CsPbBr₃ in various solvents; (e) PXRD of CsPbBr₃ and MAPbBr₃, * indicated PbBr₂ peaks.

Selectivity. A high yield of 3a, 4a and 5a can be selectively obtained under simple alterations of the reaction conditions. Apparently, 5a is of more synthetic significance towards C-C formations. Starting with 1a and 2a, in the presence of CsPbBr₃ NCs, dicyclohexylamine and 2,6-lutidine without N₂-sparging, the reaction vessel is illuminated with an LED and produces 5a in 75% yield in DCM (Table 1, entry 1). Importantly, freshly prepared solvents, removing water and stabilizer, suppresses dehalogenation but encourages 5a formation (entries 2-7).³¹ Furthermore, using N,N-diisopropyl-ethylamine (DIPEA) (entries 8-9), produces 3a in a yield of 95%, demonstrating a highly selective alkyl-halide reduction. When the amine is replaced with (5S)-(-)-2,2,3-trimethyl-5-benzyl-4-imidazolidinone, 6 an expensive co-catalyst commonly used in photoredox catalysis,³ surprisingly, the sp³-C coupling product 4a is obtained in 80% vield (entry 16). Hence, under slight changes in reaction conditions, we can selectively produce 3a, 4a or 5a. Next, we screened various amines as co-catalyst (entry 10-18). Primary amines result in no alkylation products. (entries 14-15) Our results corroborate previous findings that secondary ammonium salts are superior to their respective amines for α -alkylation.³² Overall, bis(2-chloroethyl)amine hydrochloride, provides the highest selectivity and yield, up to 96% for 5a, (entry 10) with substrate ratio (1a/2a) 1/2 (ratio exploration details in Table S2). Anaerobic conditions are not required for 5a formation. (entries 10-11; 17-18) As expected, the control experiments revealed no product in the absence of perovskite, light, co-catalyst, or base. (entries 19-22).

Table 1. Optimization of reaction condition for α -alkylation of aldehydes.^a

| Bue LED Bue LED Hex H H H H H H H H H H H H H | | | | | | |
|--|--|------------------|----------|--------------|----|----------|
| | Hex solvent, R.T. | 5a Ö | | 0 | 3a | |
| Та | Zd | ou | | -u | | u |
| Entry | Co-catalyst | Solvent | Conver- | Yield (%) b. | | |
| | | | sion (%) | 5a | 4a | 3a |
| 1 | Cy ₂ NH | DCM | >99 | 75 | - | 15 |
| 2 | Cy ₂ NH | dioxane | 90 | 45 | - | 20 |
| 3 | Cy ₂ NH | dioxanec | 90 | 55 | - | 12 |
| 4 | Cy ₂ NH | THF | >99 | 15 | 18 | 55 |
| 5 | Cy ₂ NH | THF ^c | >99 | 55 | 6 | 18 |
| 6 | Cy ₂ NH | THF ^d | >99 | 69 | - | 6 |
| 7 | Cy ₂ NH | THF ^e | >99 | 26 | 10 | 52 |
| 8f | - | THFd | 97 | - | - | 92 |
| 9 ^f | - | DCM | >99 | - | - | 95 |
| 10 | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | >99 | 96 | - | trace |
| 11 ^g | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | >99 | 96 | - | trace |
| 12 | Cy ₂ NH HCl | DCM | >99 | 85 | - | 10 |
| 13 | (n-C18H37)2NH HCl | DCM | 92 | 65 | - | 25 |
| 14 | n-C ₁₈ H ₃₇ NH ₂ HCl | DCM | 82 | trace | | 63 |
| 15 | n-C18H37NH2 | DCM | 77 | trace | - | 56 |
| 16 | 6 | DCM | >99 | 10 | 80 | trace |
| 17 ^h | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | >99 | 89 | - | trace |
| 18 ^{g,h} | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | >99 | 90 | - | trace |
| 19 ⁱ | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | 0 | - | - | - |
| 20 ^j | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | <5 | ~ | - | trace |
| 21 | - | DCM | <5 | - | - | trace |
| 22 ^k | (ClCH ₂ CH ₂) ₂ NH HCl | DCM | <5 | - | - | trace |

^{a-}Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), CsPbBr₃ (1.0 mg), Co-catalyst (20 mol%), 2,6-lutidine (1.0 mmol) and solvent (1 mL) under 455 nm LED illumination at R.T. (Note: no N₂ sparging); ^b-Yield determined by ¹H NMR; ^c-molecule sieves predried solvent; ^d-freshly distilled THF; ^e-freshly distilled THF adding 1% water; ^fDIPEA instead of 2,6-lutidine as base; ^g-with N₂-sparging; ^hMAPbBr₃ instead of CsPbBr₃; ⁱ-without light; ^j-without CsPbBr₃; ^k-without base.

Stability and TON. One of major obstacles concerning the application of Pb-halide perovskites is their instability, particularly towards moisture.^{33,34} The situation is quite distinct if Pb-halide perovskites are applied to organic synthesis. We find a surprisingly strong stability of CsPbBr3 in organic solvents indicated by observing the PL spectrum of CsPbBr3 in different organic solvents for several weeks (MAPbBr3 is less stable, Fig. S5). The good stability is also corroborated by a large TON. The CsPbBr3 remain emissive after a typical reaction (Fig. S6) indicating they likely remain catalytically active. The colloids are isolated from the previous reaction mixture via centrifuging and then re-used for a new reaction without any treatment under identical conditions. The photocatalyst remains active for at least four cycles (Fig. S7) suggesting a lower limit of the TON to be at least 52,000 (SI and Table S1). A large aliquot of water will deactivate and completely dissolve the perovskites, rendering a desired opportunity to easily separate the photocatalyst from organic products. Note that the separation of photocatalyst from photoredox reactions remains an issue using Ru/Ir or organic dyes.35

Mechanism. A proposed mechanism for these observations is outlined in Fig. 2a. Photoexcited electrons reduce **1** to form a radical **7**, which is a key step for all three products. In path I and II, **7** either extracts a hydrogen atom from a sacrificial donor (*i.e.* DIPEA) forming **3** or when a sacrificial donor is not present, self-couples producing **4**. Regeneration of the perovskite catalysts can be achieved via oxidation of the sacrificial donor in I or oxidation of an aldehyde in II. We also speculate that oxidative quenching by enamine **8** leads to radical **9** (pathway III). Iminium cation **10**

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is thus produced via a radical-radical reaction followed by hydrolysis to release the product 5 to regenerate the co-catalyst. Radical intermediates are the key components for photoredox catalysis. To further explore our proposed mechanism, radical trapping experiments were conducted with 1a and enamine 8, respectively (SI and Figure 2b). Corroborating with perovskite quenching experiment (enamine, $k_q = 2.0 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$; 1a, $k_q =$ 2.7×10^{10} M⁻¹s⁻¹, SI and Figure S8-10), the radical trapped product TM-1 and TM-2 were all isolated and confirmed by ¹H NMR from reaction I and II, while no trapped products were detected in control experiments without CsPbBr₃ (Fig. S11-14). Note that TM-2 has been previously illustrated to form from radical 9 trapped by TEMPO.³⁶ The TEMPO trapped products prove the direct formation of radicals 7 and 9 as shown in our mechanism, supporting our proposed closed-cycle mechanism. However, our observation cannot completely rule out the previous reported chain reaction mechanism using a molecular photocatalyst.37



Figure 2. (a) Proposed mechanism for perovskite catalyzed dehalogenation, sp³C-coupling and α -alkylation. (b) TEMPO trapped experiment for radical intermediate validation

Reaction Scope. Electron-donating and withdrawing tolerances were observed on α-bromo carbonyls (5b, 5c, 5e, 5f; 79 to 90% yield). The extended aromatic rings afforded the desired products 5g (85%) and 5i (82%). Simple α -bromo ester leads to a moderate alkylation yield (5h 65%, 5l 55%). Overall, aromatic aldehydes demonstrate slightly less yields, respectively. Product 5k, with 8 chiral centers was also produced with over 56% yield, exhibiting a general acceptance of our photocatalysis. Moreover, the library of product 3 and 4 was expanded. High yields of alkyl-halide reductions (3a-c, 3e above 90%, 3d 79%) with DIPEA are shown in Table 2. Selective reduction of alkyl-halide over aryl-halide is also achieved. (3e, 90%) The sp³C-coupling products 4 were also explored (4a-c, 59-80%, 4d 15%). The lower yield of 3d and 4d is likely due to the finite absorption and PL of naphthalene which interferes with the CsPbBr₃ NCs absorption, resulting in lessefficient photocatalysis.

Table 2. Scope of photocatalytic reductive dehalogenation, sp³-C couplings, and α -alkylation of aldehydes. ³⁸



Bandedge Tuning. One promising property of the Pb-halide perovskite photocatlysts is that their band structure can be easily tuned.³⁹⁻⁴¹ The excited-state redox potentials, E^* of a photocatalyst governs organic substrate activation.⁵ E^* can be defined by: $E_{ox}^* = E_{ox} - E_{00}$ and $E_{red}^* = E_{red} + E_{00}$, where E is the potential of the ground-state redox couple and close to the redox level of the conduction and valence bands, E_{00} is the energy gap between the zeroth vibrational levels of the ground and excited states and is roughly equal to the energy of the PL with error ca. 100 mV.⁴² Thus E* can be manipulated via perovskite bandedgetuning. Halide composition of $APbCl_xBr_yI_{3-x-y}$ ($0 \le x, y \le 3$) with a ratio varying on x, and y, leads to bandgaps covering from 3.2 eV to 1.5 eV.⁴³⁻⁴⁵ Such large bandedge-tuning (1.7 eV), can be easily reached via simply mixing of different ratio of halides at the initial mixing, or via anion-exchange after synthesis ^{10,46,47} Other catalysts, i.e. Ir/Ru complexes, require significant synthetic efforts to reach specific E^* values. Estimation E^* of APbCl_xBr_yI_{3-x-y} (Table S3) leads to perovskites covering almost all known noblemetal catalysts E*, implying potential for broader substrate photoactivations via perovskite.

With regards to cost-effective, operational convenience and possible scale up, it is notable to consider that our perovskite protocol: (1) only requires readily available non-noble materials, with 2-orders of magnitude lower costs than Ru/Ir catalyst; (2) presents high catalytic TON evidenced by 3-orders of magnitude higher value than Ru/Ir catalysts; (3) only requires minimum synthetic effort to produce the catalysts; (4) may activate a broader scope of organic substrates due to easy bandedge-tuning; (5) is easy-to-process since perovskites are water washable; (6) only requires visible light; (7) does not require anaerobic sparging; and (8) does not require heating or cooling.

In summary, we established a hybrid halide perovskite photocatalytic system for organic synthesis. APbBr₃ NC colloids are directly employed in organic solvents to demonstrate highlyefficient α -alkylation of aldehydes, sp³-C couplings and alkylhalide reductions. High TON and low-cost garners a significant progress of the current perovskite system. Easy and wide bandedge-tuning of perovskites NCs ripostes the key challenge to activate broader range of organic substrates requiring different

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energy level from enamine intermediates, alkenes, carbonyls, halides, acetic acids to amines *etc.* for C-C, C-O and C-N formations. The potential broad application of this cost-effective, easily-prepared, highly-efficient and band-tunable hybrid halide perovskites may bring in new insights in photocatalysis of organic reactions.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>. Materials and methods, Fig. S1-S44, Table S1-S3, synthesis procedures, and ¹H and ¹³C NMR spectra.

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Notes

The authors declare the following competing financial interest(s): A provisional patent application has been filed on the perovskite catalysts and their use in photocatalytic organic synthesis.

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