Lead halide perovskites for photocatalytic organic synthesis

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Nature is capable of storing solar energy in chemical bonds via photosynthesis through a series of C–C, C–O and C–N bond-forming reactions starting from CO$_2$ and light. Direct capture of solar energy for organic synthesis is a promising approach. Lead (Pb)-halide perovskite solar cells reach 24.2% power conversion efficiency, rendering perovskite a unique type material for solar energy capture. We argue that photophysical properties of perovskites already proved for photovoltaics, also should be of interest in photoredox organic synthesis. Because the key aspects of these two applications are both relying on charge separation and transfer. Here we demonstrated that perovskites nanocrystals are exceptional candidates as photocatalysts for fundamental organic reactions, for example C–C, C–N and C–O bond-formations. Stability of CsPbBr$_3$ in organic solvents and ease-of-tuning their bandedges garner perovskite a wider scope of organic substrate activations. Our low-cost, easy-to-process, highly-efficient, air-tolerant and bandedge-tunable perovskites may bring new breakthrough in organic chemistry.
The intentional construction of organic compounds via cost-effective and efficient photocatalysis is highly desirable. Remarkable advances in artificial C–C, C–O, and C–N bond formations have been made, including the development of protocols to merge photoelectrochemical catalysis with organic, transition-metal catalysis, and inorganic semiconductors. However, many current catalysts require high-cost noble metals; complicated synthetic preparations; air-free reaction conditions; or demonstrate moderate activity and are thus not desirable. A need to develop easy-to-produce, economical, effective and highly-tolerant photocatalyst for a broad scope of chemical bond formations, remains a significant challenge. Of the potential photoactive materials, Pb-halide perovskites APbX₃ are an attractive candidate. They have shown promise for low cost solar energy conversion (e.g., they have strong light absorption, long excited state lifetimes, efficient separation and transport of opposite charge carriers). As a result, revolutionary advances have been claimed in perovskite photovoltaics, i.e. PCE has reached greater than 24.2% in only a few years of development.

Given the widespread success of perovskite in both efficient charge separation and electron-hole diffusion (length > 175 nm), we recently questioned whether it might be possible to apply this unique material that has been proved in photovoltaics towards highly efficient photocatalytic organic synthesis. In photovoltaics, the absorption of photons induces the creation of electron-holes, while in photocatalysis, the equivalent is the production of reducing/oxidizing charges that can drive the desired chemistry. For photocatalysis, such reducing/oxidizing equivalents (excited electrons/holes) should live long enough and be transported efficiently to a catalytic site where chemistry occurs (i.e., at the photocatalyst surface). Therefore, photophysical properties of Pb-halide perovskites demonstrated for photovoltaic applications, also should be of interest in photocatalytic organic synthesis.

We recently demonstrated that the intrinsic surfaces of MAPbI₃ and MAPbBr₃ perovskites have low surface recombination velocities and indicate an intrinsic of low surface defect density that would otherwise hinder surface chemical reactions needed for photocatalytic systems. Our initial exploration of perovskites towards photocatalytic α-alkylation of aldehydes successfully proved that C–C bond formation reactions are efficiently achievable. Other organic reactions focusing on styrene polymerization, benzenethiol dimerization and C–P bond formation between tertiary amines and phosphite esters were also reported. We also note that a perovskite-based photocatalyst cell, perovskite/TiO₂ or NiO₄/perovskite/TiO₂ is report to photooxidize benzyl alcohol or activate C(sp³)-H bond, although the yield is low, ranged from 0.016% to 0.73%.

Perovskite’s size effect. The perovskite colloids, P₁, described above are readily synthesized according to previous report via direct mixing of readily available low-cost starting materials, PbX₂ with CsX, in an open vial under bench-top conditions (Supplementary Fig. 1). The resulting gram-scale emissive perovskite colloids exhibit a broad size-distribution, ca. 2–100 nm (Fig. 2a). The observation together indicates a bandgap energy of 2.4 eV that well matches the bulk CsPbBr₃ bandgap. The synthesized colloids are too large to be in the quantum-confinement regime (Fig. 2a). Thus, for the system we are considering most colloids within the ensemble are larger than the Bohr radius, and hence the bandbends are determined by bulk bandbends and quantum-confinement effects do not contribute.

In contrast, using a high temperature synthetic method, we also synthesized size-controlled CsPbBr₃ NCs (P₂ 14 nm, λₘₚ = 521 nm; P₃ 9 nm, λₘₚ = 515 nm; P₄ 6 nm, λₘₚ = 508 nm; P₅ 4 nm, λₘₚ = 467 nm, Fig. 2b–d and Supplementary Fig. 2). As shown in Fig. 2d, these NCs show a blue-shift probably due to quantum confinement. The photocatalytic ability has also been explored in the same reaction condition. In C–H activation, at the early stage of the reaction, we find that smaller size NCs, i.e. P₂–P₄ show a higher initial reaction rate compared to the original synthesized P₁ NCs (Supplementary Fig. 3). However, small size NCs’ catalytic reactivity diminished quickly. When breaking a C–Br bond to form 1a, the reaction yield is recorded as 54–64% using P₂–P₄ in less than 40 min, and longer reaction time leads to a marginal increase of the yield of 1a. Much lower yield, ~8% was observed within P₅ probably due to a significant blue-shift leading to less visible absorption. Whereas using P₁, the reaction rate is slower, however, the yield continuously increases and reaches 85% in ca. 5 h.

We suspect that small size NCs have higher surface area-to-volume ratio (Supplementary Table 9), hence a faster rate at the early stage. However, detrimental effects, i.e. moisture residue in solvent are inevitable. Such effects are more prominent on small size NCs than P₁. We assume if the desired photocatalysis is slower than perovskite decomposition, the reaction yield may be of significant discrepancy between small and large size NCs. Such assumption is corroborated with reaction 1a described above. In contrast, if the decomposition is not prominent, the yield

Results

General acceptance of perovskites for organic synthesis. Perovskite colloidal suspension (CsPbX₃; E_CB = –1.2~–1.4 V, E_VB = +0.6~+1.5 V, all vs SCE; CB: conduction band; VB: valence band) are effective catalysts for several fundamental organic reactions under visible light as shown in Fig. 1. Direct C–C bond formations are observed via C–H activation of aldehydes (1a, 1b) or tertiary amines (1c, 1d). The scope of the former reaction is not only limited on previously explored C–Br weaker bonds, but also covers stronger C–Cl bond. The absence or presence of oxygen is the key to lead to chain-extension product (1e) or an unexpected cyclization reaction (1d). C–N bond formations via direct N-heterocyclizations forming pyrazoles (2a–f) and pyrroles (2g–i), critical reaction for pharmaceutical development, are realized in high yield with perovskite at room temperature. C–O bond formation via aroyl-esterification (3a–f) was achieved with a Ni co-catalyst. The respective reaction conditions are also optimized with regards to solvents, types of perovskites, air-tolerance, co-catalysts, and reaction time, etc. (see Supplementary Tables 1–8 for details). Catalyst loading has also been explored (Supplementary Tables 1–7) and respective minimum loading for typical reactions of ~0.1–0.5 mmol has been listed in Fig. 1. These reactions result in respective products in moderate to high yields without need for anerobic sparging. The scopes of each aforementioned reaction were explored with various functional groups. (Fig. 1 and “Methods” section for details) As expected, control experiments reveal no product in the absence of photocatalyst or light.
1. C–C bond formation via C–H activation

![Chemical structure](image)

2 equiv 1 equiv

Blue LED CsPbBr₃ (1 mg)
(ClIC₃H₇CH₂Cl)₂NHCl (20 mol%) 2,6-lutidine (2 equiv) CH₂Cl₂, air

2a, 1b

1a: R¹ = H, X = Br, 84%
1b: R¹ = Cl, X = Cl, 52%

2. N-Heterocyclization

![Chemical structure](image)

1.5 equiv 1 equiv

Blue LED CsPbBr₃ (1 mg)
Cs₂CO₃ (1 equiv) Et₂OAc, air

2a–2f

2a, R¹ = Ph, R² = Ph, 84%
2b, R¹ = p-NO₂C₆H₄, R² = Ph, 84%
2c, R¹ = 3-Coumarin, R² = Ph, 89%
2d, R¹ = Ph, R² = p-BrC₆H₄, 83%
2e, R¹ = Ph, R² = p-NCC₆H₄, 90%
2f, R¹ = 2-Np, R² = Ph, 82%

3. C–O cross-coupling

![Chemical structure](image)

1 equiv 2 equiv

Blue LED CsPbBr₃ (2 mg)
TFA (1 equiv) CH₂Cl₂, O₂

1a, 1b

Blue LED CsPbBr₃ (1 mg)
CH₂Cl₂, N₂

1c, 85%

Blue LED CsPbBr₃ (1 mg)
TFA (1 equiv)

1d, 76%

Fig. 1 The library of C–C, C–N, and C–O bond formation reactions and respective yield. (Yields of 1a, 1c, 1d, 2a, 2g, 3a are the average yields of three reactions, see Supplementary Table 8; Inset: perspective view of 1d’s single crystal structure with the thermal ellipsoids drawn at 50% probability level and the H atoms omitted for clarity.)

Discrepancy is less obvious. In fact, in 2a, perovskite is stable in a pre-dried non-halide solvent ethyl acetate (Supplementary Fig. 4). 2a is produced in 86% yield with P2 in 2 h, 87% using P1 in 6 h (Supplementary Fig. 3). Overall, small size NCs, in general, promote a faster reaction rate, but not necessarily a higher yield unless presenting in a perovskite friendly reaction environment. Considering synthesis merits, large size NCs, in general, provide higher yield although a longer reaction time in a scale of 6 h or higher is required.

Stability and reaction condition tolerance. Pb-halide perovskites’ photovoltaic performance perishes over moisture,28,29, impeding the wide commercial application of such materials as solar cells. The stability is quite distinct if perovskites are to be applied to organic synthesis in which more critical parameters may influence the stability of perovskites, i.e. solvent type, ions, acidity, etc., and further manipulate the catalytic ability. Thus, these parameters are evaluated individually for a better understanding of perovskite photocatalysis. A quite strong stability of P1 in organic solvents was indicated by no obvious PL changes of CsPbBr₃ for several weeks in less polar organic solvents.28,30 (Note that P1 is not stable in polar solvents, i.e. acetone, acetonitrile, DMF, DMSO, Supplementary Fig. 4). However, P2–P5 are less prominent and significant PL diminishing is observed. (Supplementary Fig. 2) Interestingly, under the irradiation of LED, PL blue-shift of P1 in CH₂Cl₂ are observed in 24 h. (Fig. 2e) Such changes are significantly magnified on P2–P5 as shown in Fig. 2e and Supplementary Fig. 5, absorption and PL blue-shift within in 1 h, whereas no obvious PL changes are observed in non-halide solvents. This observation may be attributed to a photoinduced fast halide exchange for CsPbBr₃ with CH₂Cl₂ as previously reported16,30.

Next, we evaluate the ion effect in perovskites’ photocatalysis. Perovskite is reported to sensitive to both inorganic cations and anions.31–34 In our photocatalytic setup, co-catalyst (CIC₃H₇CH₂Cl)₂NH₄Cl in reaction 1a, leads to an initial PL blue-shifted due to anion-exchange forming CsPbBr₃Cl₃-x, confirmed by XRD (Fig. 2f). It is interesting to point out that co-formation of Br ion during reaction 1a, may further exchange with the CsPbBr₃Cl₃-x and stabilize the perovskite NCs. Such
stabilization is evidenced by the after-reaction catalyst characterization in which XRD indicates that the isolated photocatalyst solid was corresponding to CsPbBr3 and surprisingly, no peak has been assigned to CsPbCl3 (Fig. 2f). This is probably because the co-formation Br ions are in chemical equivalency and its concentration is significantly higher than that of Cl. Therefore, a Br compensated and stabilized CsPbBr3 photocatalyst system is thus observed. (Supplementary Fig. 6) In contrast, reaction 1b employing Cl-substrates leads to a fully-exchanged CsPbCl3 after reaction (Fig. 2g). Overall, perovskite shows a much better stability during the reaction 1a, in which the NCs can be isolated from the previous reaction mixture via centrifuging and then re-suspended for a new reaction under identical conditions for at least four cycles with slightly PL blue-shift, whereas small NCs’s recycling ability is limited (Supplementary Fig. 3). As comparison, when free halide anions are absent, for example in reaction 2a in EtOAc solution, the overall stabilities for P1 and P4 are enhanced and result in an improved recyclability in such perovskite friendly environment (Supplementary Figs. 6 and 7).

Acidity or free protons in perovskite reaction mixture may play a role in organic synthesis. For instance, carboxylic acids such as propionic acid, benzoic acid or trifluoroacetic acid (TFA), were employed as the co-catalyst (1c and 1d) or as a substrate (3a–3f). Thus, we first measured the PL for perovskite NCs with different acids to elucidate the tolerance of acidic conditions. Interestingly, as shown in Fig. 2h and Supplementary Figs. 8 and 9, a PL enhancement of P1 was observed upon the addition of benzoic acid, propionic acid, and also TFA (see Supplementary Movie 1). This is corroborated with previously observed PL enhancement using thiophenol16, phosphoric acid35 etc. The PL enhancements are probably because carboxylic acid function as the capping ligand by the strong hydrogen bonding with surface halide ions35 and may also account from a strong interaction between carboxylic acid and Pb atoms, indicated by Tan et al.36. Acid binding with defects on perovskite may also lead to an enhanced

Fig. 2 Characterization and spectroscopy studies of photocatalysts. a TEM of CsPbBr3 P1, b P3, c P4, d UV-vis and PL spectra of CsPbBr3 P2–P5, e PL spectra for P1 and P4 in CH2Cl2 as prepared and after LED irradiation for 24 h and 1 h, respectively, f XRD of as-prepared CsPbBr3 P1, isolated from the reaction 1a before and after irradiation, respectively, g the corresponding XRD for reaction 1b, h PL spectra of P1 in THF with addition of TFA, i PL spectra of CsPbBr3 NCs, Ir(ppy)3, CdSe QDs and Ru(bpy)3Cl2 in air or N2-saturated solutions. Source data are provided as a Source Data file.
N2-sparging. In stark contrast, molecular photocatalyst necessitates air-free reaction conditions. The key difference here is that the perovskite NCs likely undergo faster quenching from the organic substrates, while quenching from air is negligible. (Fig. 2i and Supplementary Fig. 10) The reverse is true for most cases of molecular catalysts – quenching is substantial and competitive with the catalytic reactions, leading to poor catalytic results. Hence, yields of reaction 1c and 1d as shown in Supplementary Tables 3 and 4, indicating that a high PL of the photocatalyst may increase the catalytic conversion. Therefore, non-halide organic acid may not only stabilize the perovskite NCs, but also may increase the overall catalytic efficiency for respective reactions.

**Key catalytic parameter comparison with other photocatalyst.** Air-tolerance is important for the practical end-use of chemical synthesis. One distinct advantage of our colloidal system is that the organic reactions observed here occur without the need for N2-sparging. In stark contrast, molecular photocatalyst necessitates air-free reaction conditions. The key difference here is that the perovskite NCs likely undergo faster quenching from the organic substrates, while quenching from air is negligible. (Fig. 2i and Supplementary Fig. 10) The reverse is true for most cases of molecular catalysts – quenching is substantial and competitive with the catalytic reactions, leading to poor catalytic results. Hence, yields of reaction 1c and 1d as shown in Supplementary Tables 3 and 4, indicating that a high PL of the photocatalyst may increase the catalytic conversion. Therefore, non-halide organic acid may not only stabilize the perovskite NCs, but also may increase the overall catalytic efficiency for respective reactions.

| Photocatalysta | Yield (%)b | TON (based on CsPbBr3)c |
|----------------|------------|-------------------------|
|                | 1a | 1c | 1d | 2a | 3f | 1a | 1c | 1d | 2a | 3f |
| CsPbBr3 P1 | 84 | 85 | 76 | 84 | 70 | 9,100 | 830 | 280 | 380 | 33 |
| Ru(bpy)3(PF6)2 | Trace | 60 | 25 | Trace | N.R. | - | 60 | 25 | - | - |
| Ir(ppy)3 | 79 | N.R. | N.R. | 63 | 65 | 79 | - | - | - | 63 | 33 |
| CdSe QDs (525 nm) | Trace | Trace | N.R. | N.R. | N.R. | - | - | - | - | - |

a bipy 2,2'-bipyridine, ppy ortho-metalted 2-phenylpyridine
b average yield using for P1
c details in Supplementary Note 2

PL performance according to Zhu et al.37. The maximum PL was observed using TFA at a concentration of ca. 6.5–13 mM, more acid leads to a diminishing PL probably because large number of protons may start to initiate a deactivation process. Interestingly, such optimized TFA concentration also leads to a maximum product yield of 1c and 1d as shown in Supplementary Tables 3 and 4, indicating that a high PL of the photocatalyst may increase the catalytic conversion. Therefore, non-halide organic acid may not only stabilize the perovskite NCs, but also may increase the overall catalytic efficiency for respective reactions.

**Mechanism.** Oxygen may be of an essential component in certain photoredox reactions. For instance, in Fig. 3a, radical addition product 1c is achieved in nitrogen atmosphere while in a similar setup, air or oxygen atmosphere produces a ring-closure 1d which is crystal structure provided in Fig. 1. Oxygen is found to be the key reagent as the hydrogen atom acceptor that further induced the C–H activation on phenyl rings39,40. As shown in Fig. 3, the reaction mechanisms are proposed in which the key radical intermediates have been investigated. Upon Stern–Volmer studies (Supplementary Figs. 11–17), perovskite PL quenching by 1d-A was observed (kq = 3.6 × 108 M–1 s–1, details see Supplementary Fig. 12 and Supplementary Note 3) and resulted in 1d-B radical in the presence of oxygen. Intermediate 1d-B and 1d-C have been verified via radical trapping experiment employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger, through LC-MS (Supplementary Figs. 19 and 20). In the absence of oxygen, radical 1c-B is also confirmed by TEMPO-trapped product (Supplementary Fig. 18) and further verified by the self-coupling 1c-C via 1H NMR. It is worth mentioning that the
presence of air leads to more 1c-C formation and ultimately diminishes the yield of 1c.

Figure 3b shows the proposed mechanism of C–N formations, in which both oxidative (ET, 2a-A) and reductive quenching product (HT, 2a-B) in reaction 2a have been trapped by TEMPO (either observed via \(^1\H\) NMR or LCMS), indicating a strong charge separation and transfer ability induced by perovskite. This pathway is similar to our previous mechanism exploration in α-alkylation of aldehydes. Radical coupling between 2a-A and 2a-C leads to the intermediate of 2a-D. Then C–N formation via intramolecular cyclization and a final dehydration leads to the pyrazole product 2a. In contrast, the radical formation from 2g-B via direct HT has not been observed, instead 2g-C was verified via radical-trapping, likely demonstrating a different mechanism of pyrrole formation as shown in Fig. 3b.

To further elucidate the reaction mechanism, electrochemical studies were conducted. (Supplementary Figs. 24–31) According to the comparison between redox potentials of the key substrates and the band energy of perovskite, the respective driving force is listed in Fig. 4. Driving force for HT in reaction 1c, 1d and 2a is observed among ~0.1 to 0.3 eV, consistent with the Stern–Volmer quenching results (Supplementary Figs. 11–17) as well as the mechanistically verified intermediates in Fig. 3. However, 2g-B disfavors HT due to a more positive oxidation potential (\(E_{\text{red}} = 1.42\) V vs SCE), corroborating with the previous observation that direct radical forming from 2g-B is difficult, unlike reaction 2a pathway. Moreover, driving force for ET is also listed from ~0.2 to 0.5 eV, confirming our discussion on ET in Fig. 3. However, noticeable exception, 2,4'-dichloroacetophenone, though presenting a more negative reduction potential (\(E_{\text{red}} = -1.47\) V vs SCE), still reacts to form respective pyrrole. We postulate that in-situ band-tuning of perovskite may play a role here and is discussed below.

Unique band-tuning of perovskite. As discussed above, the perovskite NCs P1 are too large to be in the quantum-confinement regime and the majority of the NCs within the ensemble are larger than the Bohr radius. Thus, the band energy of our photocatalyst, analogs to excited state redox potentials, \(E^*\)
in molecular catalyst, is determined by the bulk bandedges. Band-tuning is achievable by simply mixing of different ratio of halides. We also observed that in-situ ion exchange using P1 results in band-tuning (Fig. 5a). In theory, as shown in Fig. 5b, c the bandedges of perovskite after tuning covers most of the $E^*$ of the known Ru or Ir molecular photocatalysts.

The band-tuning is of critical importance for a photocatalyst to activate different types of substrates. For example, C–O formation reaction 3 is also proposed and shown in Supplementary Fig. 32 similar to previously reported mechanism. It is reported that energy transfer from triplet excited state of Ir photocatalyst is the key for Ni complex activation thus resulting in an efficient reductive elimination for C–O bond formation. Triplet energy ($E_T$) exploration from Ir(ppy)$_2$ derivatives via modifying the substitution group on ppy ligand demonstrated that a higher correlation between $E_T$ and the production yield. Specifically, a higher $E_T$ results in a higher yield. As shown in Fig. 5d, in our perovskite system, 3f is produced in trace amount if CsPbBr$_3$ is employed with dtbbpyNiBr$_2$ co-catalyst, comparing to 78% with dtbbpyNiCl$_2$. While in Ir photocatalysis, the different halides on Ni co-catalyst only play a marginal effect. We suspect that an in-situ ion-exchange from NiCl$_2$ may result in a blue shift of perovskite, similar to the increasing $E_T$ in Ir system, thus leading to a significantly higher yield of 3f using co-catalyst dtbbpyNiCl$_2$. To further confirm this hypothesis, we have conducted a systematic band-tuning experiment to demonstrate the correlation between the bandedges and the yield of 3f. In a typical experiment, perovskite CsPbBr$_3$ is employed with NiBr$_2$ co-catalyst, but tuned using a reported agent, i.e. trimethylsilyl chloride (TMSCI). We find that shifting the bandgap to higher values, by mixing with chloride to form CsPbCl$_x$Br$_{3-x}$, increases the yield of 3f, similar to elevate $E_T$ in Ir system. However, more Cl component is not always beneficial for this type of reaction. As shown in Fig. 5a, PL intensity is significantly lower when Cl is incorporated into perovskite. Higher bandgaps (shorter PL peak wavelengths) resulted in a lower yield, and is likely tied to the lower PL quantum efficiency that indicates a competitive carrier trapping mechanism. Overall, a maximum yield of 85% was obtained when the PL peak corresponds to 498 nm (Supplementary Table 7). This observation illustrates that the intentional band-tuning of perovskite NCs may activate previously non-reactive substrates.

Furthermore, band-tuning may also result in an absolute discrepancy in photo-activation. It is widely accepted that the C–Cl bond are stronger than C–Br and hence harder to activate. Surprisingly, in reaction 2j in Fig. 5d, α-chloroketone is observed to react to form 2j in dioxane in a yield of 67% while α-bromoketone is almost non-reactive at all. We assume that the band energy of CsPbBr$_3$ is not adequate to activate either Cl or Br-substrates in dioxane. However, ion-exchange may not only occur between CsPbBr$_3$ and CH$_2$Cl$_2$ as previously reported, but may also between CsPbBr$_3$ and suitable organic Cl-substrates. Interestingly, CsPbCl$_3$ was confirmed by XRD after reaction. (Supplementary Fig. 33) Cl-substrate is the only Cl source and hence is activated in this type of reaction. Hence CB of photocatalyst is thus moved higher, simultaneously the reduction potential of the substrate moves in a reverse direction (Fig. 5b), overall making the ET possible and finally resulting in the pyrrole formation. This is also corroborating with the observation that, if reaction 2j was conducted in CH$_2$Cl$_2$, CsPbBr$_3$ NCs may first initiate ion-exchange with the solvent hence shift band energy, and finally catalyze both Br and Cl-substrates towards 2j.
formation. This result demonstrates that in-situ band-tuning of perovskite NCs may provide unexpected activity towards previously unachievable substrates.

Discussion
In summary, a general acceptance of perovskite nanocrystals for organic reactions has been demonstrated. C–C bond formations via C–H activation, C–N, and C–O formations via N-heterocyclizations and ary-esterifications can be achieved with moderate to high yields. Large size perovskite NCs with band energy determined by bulk CsPbX₃, in general provided higher yield for rate to high yields. Large size perovskites NCs with band energy reactions.

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Synthesis of perovskite CsPbBr₃. P1. CsPbBr₃ NCs were synthesized by the modification of the method reported¹⁷,²⁵. First, two precursor solutions are prepared in advance: 2.0 mol CdBr dissolved in 2.0 mL H₂O and 2.0 mol PbBr₂ dissolved in 3 mL DMF, respectively. Then, to a vigorously stirring mixture of 500 mL hexane, 8 mL oleic acid and 1.5 mL n-octylamine, the PbBr₂ DMF solution and CdBr₂ solution are added dropwise. Along with mixing, an emulsion forms and the solution color turns from clear to slightly white. After that, acetone (400 mL) is added to break-up the emulsion. The CsPbBr₃ NCs are isolated by centrifugation at 2000 rpm for 2 min to discard large particles, and then 7900 rpm for 10 min to afford CsPbBr₃. P1.

Synthesis of CsPbBr₃-P1-oleicamine. Use the very similar method with the synthesis of Perovskite CsPbBr₃ P1, except the using of oleyamine instead of octylamine.

Colloidal CsPbBr₃ P2–P5. CsPbBr₃ P2–P5 NCs were synthesized according to the previously reported method⁵¹. First, Cs₂CO₃ (0.814 g) was loaded into 100 mL 3-neck flask along with oleic acid (2.5 mL) and octadecene (40 mL) and dried under vacuum for 1 h at 120 °C. Then, Cs₂CO₃ was injected (0.5 mL) and then OA (0.5 mL) was injected at 100 °C under N₂. After complete solubilization of PbBr₂, the temperature was raised to a desired value, and the prepared Cs-oleate solution (0.4 mL, 0.125 M in ODE) was quickly injected and, 5–10 s later, the reaction mixture was cooled by immersion in an ice-water bath. After centrifugation at 5000 rpm for 5 min to discard the precipitates, a bright yellow-green colloidal solution was obtained. The synthesized CsPbBr₃ NCs are precipitated by adding 6 mL n-butanol and then centrifuged at 12000 rpm.

Synthesis of CsPbBr₃-Xₐ X = Cl, F. First, the colloidal CsPbBr₃ are prepared in CH₂Cl₂. Subsequently, the different volumes of trimethylsilyl chloride (TMSCl) or trimethylsilyl iodide (TMSI) DCM solution is dropped into the CsPbBr₃ solution until the desired emission peak position is achieved.

Photocatalytic organic synthesis procedure. In a typical synthesis, for instance 1a and 1b, to a 4 mL vial, CsPbBr₃ NCs P1 (1.0 mg), the corresponding bromide or chloride (0.5 mmol, 1.0 equiv.), 3-phenylpropanal (1.0 mmol, 2.0 equiv.), 2,6-lutidine (1.0 mmol, 2.0 equiv.), bis(2-chloroethyl)amine hydrochloride (0.1 mmol, 0.2 equiv.), and 2 mL CH₂Cl₂ were added and then stirred under the irradiation with a 12 W 455 nm Blue LED lamp, distance ~8 cm. After 5–12 h, the mixture was poured into water, and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with water, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, Hexane/EtOAc = 10:1) to afford 1a or 1b. For 1H NMR and 13C NMR spectra of all compounds see Supplementary Figs. 34–58. Full experimental details can be found in the Supplementary Methods.

Data availability
The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information file. The X-ray crystallographic coordinates for structures of 1d has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1889861. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The source data underlying Figs. 2, 4 and 5, and Supplementary Figs. 2, 3, 5, 7–17, 24–31 and 33 are provided as a Source Data file.

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Methods
General considerations. Commercial reagents were purchased from Sigma Aldrich and TCI America. Additionally, aldehydes were distilled prior to use. Tetrahydrofuran was distilled under N₂ over sodium benzenophenonetetraethyl. All other solvents were purified by passage through columns of activated alumina. Two batches of Cds Quantum Dots with nanoparticle concentration of 50 μmol/L in hexane with emission peak at 525 nm (particle size 2.8 nm) and 550 nm (particle size 3.5 nm) were purchased from Strem Chemicals. Silica gels (230–400 mesh) used for chromatography were purchased from Sorbent Technology. 1H NMR and 13C NMR, respectively. All coupling constants (J) are reported in hertz (Hz). Tetrahydrofuran was distilled under N₂ over sodium benzophenoneketyl. All other reagents were purchased from Sigma-Aldrich as the reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The potential values obtained in reference to Ag/AgCl were converted to the saturated calomel electrode (SCE) in order to directly compare with literature. All solutions were purged with N₂ for 20 min before experiments.
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