The Synergy between the CsPbBr₃ Nanoparticle Surface and the Organic Ligand Becomes Manifest in a Demanding Carbon-Carbon Coupling Reaction

Ignacio Rosa-Pardo, Carla Casadevall, Luciana Schmidt, Miguel Claros, Raquel E. Galian, * Julio Lloret-Fillol, * Julia Pérez-Prieto *

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Experimental Procedures

1. Experimental Section

1.1. Materials and physical methods

Chemicals. Cesium bromide (99.999 %, Sigma Aldrich, USA), lead bromide (99.999 %, Sigma Aldrich, USA), europium(II) bromide (99.99 %, Alfa Aesar, Germany), dodecylamine (98 %, Sigma Aldrich, USA), myristic acid (≥99 %, Sigma Aldrich, USA), *N*,*N*-dimethylformamide (99.8 %, VWR, USA), dimethyl sulfoxide (≥99 %, VWR, USA), toluene anhydrous (99.8 %, Sigma Aldrich, USA), benzyl bromide (98 %, Sigma Aldrich, USA), 4-bromobenzyl bromide (98 %, Sigma Aldrich, USA), 4-methoxybenzyl bromide (97 %, Fluorochem, UK), 4-chlorobenzyl bromide (97 %, Sigma Aldrich, USA) and 4-*tert*-butylbenyl bromide (97 %, Sigma Aldrich, USA).

Synthesis of colloidal CsPbBr₃ perovskite nanocrystals: 200 μ L of a precursor solution containing equimolar concentrations of cesium bromide (CsBr) and lead bromide (PbBr₂) in a 9:1 dimethylformamide/dimethylsulfoxide mixture were mixed with DDA (0.053 mmol). This solution was added dropwise to a toluene solution of myristic acid (MA, 0.709 mmol). Centrifugation of the solution at 5000 rpm for 5 min led to a precipitate, which was redispersed in 2 mL of toluene for further use.¹



Figure S1. Schematic illustration of the ligand-assisted reprecipitation technique carried out for the preparation of CsPbBr3 perovskite nanocrystals.

Characterization

Absorption measurements. UV-visible spectra were recorded at room temperature using quartz cuvettes of 1 cm x 1 cm in a UV-visible spectrophotometer JASCO V-670.

Luminescence measurements. Photoluminescence spectra were measured on an Aminco Browman series 2 Luminescence spectrometer, equipped with a xenon lamp (150 W). AB2 software (version 5.5) was used to register the data. Time-resolved PL were measured using a Compact fluorescence lifetime spectrometer C11367, Quantaurus-Tau. Fluorescence lifetime software U11487 was used to register the data. All of the data of PL decay of perovskite dispersed in toluene were acquired using 1 cm × 1 cm path length quartz cuvettes and light-emitting diode excitation wavelength of 365 nm. The PL decay of colloidal perovskite nanoparticles were fitted with a triexponential function. The average lifetimes (τ_{av}) were calculated as $\tau_{av} = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$, where τ_i are the decay times and α represents the amplitudes of the components, values obtained from the fitted PL kinetic decay traces.



Figure S2. Absorption and emission spectra of colloidal CsPbBr₃ perovskites in toluene at room temperature.

Transmission electron microscopy. Transmission electron microscopy (TEM) was performed on a JEOL 1010 microscope operated at 100 keV.

Quantum yield measurements. The photoluminescence (PL) quantum yields were measured using a Hamamatsu C9920-02 absolute PL quantum yield measurement system with monochromatic light source (150 W) and integrating sphere. All of the data were acquired using 1 cm \times 1 cm path length quartz cuvettes, at room temperature, using an excitation wavelength at 365 nm.

In-house developed parallel photoreactor²

Light source: The reactions were performed using Royal-Blue (λ = 447±10 nm) LUXEON Rebel ES LED, mounted on a 10mm Square Saber - 1030 mW@700mA (Datasheet: <u>https://www.luxeonstar.com/assets/downloads/ds68.pdf</u>) as a light source.

Temperature Control: Reaction temperature was controlled by a high precision thermoregulation Hubber K6 cryostat. Likewise, to guarantee a stable irradiation the temperature of the LEDs was also controlled and set up at 22 °C.

The reactions have been carried out in two different in-house parallel High Throughput Screening (HTS) photoreactors with capacity to set up to 25 and 48 reactions, respectively, under high intensity irradiation. These unique HTS platforms allow for a tight control of the light intensity (Royal-Blue; λ = 447±10 nm) and the temperature of the reactions. The **25 position photoreactor** is operable at 2-15 mL reaction volumes for each reaction (millimole scale – scale up), whereas the **48 position photoreactor** ranges from 100-250 µL reaction volumes (micromole scale - screening).





Figure S3. (Top) In-house developed 24-well parallel photoreactor used for scale-up (isolated yields). (Bottom) In house developed 48-well parallel photoreactor used for screening and optimization of the catalytic conditions.

Electrochemical measurements

Electrochemical experiments were carried out with a VSP potentiostat from Bio-Logic, equipped of the EC-Lab software. Cyclic Voltammograms (CV) were recorded at 2 mM concentration of the substrate by using tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (0.1 M) in anhydrous acetonitrile (MeCN), purchased from Sigma-Aldrich and stored in a glove box. The experiments were carried out under N₂ atmosphere in a three-electrodes customized electrochemical cell, using a glassy carbon (GC) working electrode ($\emptyset = 3$ mm) and a Pt wire as a counter electrode. A silver wire, immerged in the same electrolyte solution and separated from the main solution by a porous tip, was used as a pseudo-reference to avoid water contamination in the organic solvent coming from aqueous electrodes. Ferrocene (Fc) was added to the solution as an internal standard at the end of each experiment. In our conditions, the Fc^{+/0} redox couple appears at E_{1/2}= +0.71 V in 0.1 M TBAPF₆/propylene carbonate electrolyte (E_{1/2}= +0.38 V in 0.1 M TBAPF₆/CH₃CN³) against a Saturated Calomel Electrode (SCE). All the potentials reported in the manuscript are then referenced versus Standard Hydrogen Electrode (SHE), obtained correcting the observed redox potentials regarding Fc and then adding +0.244 V to the potential values vs. SCE. Cyclic Voltammograms are recorded at scan rate v = 0.1 V s⁻¹.

UV-Vis spectroscopic studies. UV/VIS spectra were measured with an Agilent 8453 diode array spectrophotometer (λ = 190–1100 nm). All experiments in a 0.5 cm UV-Vis cell containing the CsPbBr₃ perovskite (1.44 mM final concentration) in toluene were performed at 25 °C temperature controlled with a cryostat. Corresponding additions of Et₃N (0,35 M) and/or benzyl bromide (35 mM) were carried out regarding the experiment performed.

General procedure for the photocatalytic carbon-carbon coupling of benzyl bromides. The photocatalytic reactions were prepared inside a nitrogen filled glovebox and conducted in a 1 mL vial under vigorous stirring using an orbital shaker in a photoreactor with blue LEDs (447 nm) during 20 h at 30 °C, unless otherwise is indicated. The substrate (200 μ l of a stock solution, final concentration 34 mM) were dissolved in ethyl acetate (60 % v/v) or toluene, followed by the addition of the electron donor (DIPEA, 20 equivalents) and the colloidal CsPbBr3 nanocrystals (200 μ l of the stock solution were added to the reaction vial, final concentration 1.44 μ M) until a final reaction volume of 500 μ l. Immediately after the reaction finished, biphenyl (1 eq.) was added as internal standard and the crude of the reaction was centrifuged at 1500 rpm during 15 minutes. Ethyl acetate was added to the reaction crude to extract the organic compounds and the procedure was repeated again. The supernatant was subjected to GC analysis to determine the conversion of substrates and the yield of the desired product (Table 1). The reported yield of C-C homocoupling product was an average of at least two runs. The pellet was redispersed in toluene to obtain the colloidal perovskite after the photocatalytic cycle.

General procedure for homo- and hetero-coupling products formation. A solution of the different benzyl bromides compounds **1a-5a** (0.8 mL final volume of the mixture, 0.068 mmol and 0.034 mmol of each in hetero-coupling reactions), colloidal **CsPbBr₃** (final concentration 1.44 μ M) and degassed DIPEA (240 μ L, 1.37 mmol) in toluene (final reaction volume of 2 mL) were loaded into 10 mL gas-tight crimped vials containing glass beads. The vials were sealed with a septum and placed in the photoreactor at 30 °C. After irradiating (447 nm) the vials for 48 h, the crude of the reaction was transferred to a separatory funnel, followed by the addition of water (15 mL) and diethyl ether (15 mL). The aqueous layer was extracted with Et₂O (3 x 15 mL), and the combined organic extracts were washed with brine (15 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the crude material was purified via preparative chromatography TLC. The concentration of the perovskites was calculated using the molar coefficient reported for CsPbBr₃ nanocubes of 11 nm (3.5 10⁶ M⁻¹ cm⁻¹).

A 20:1 TEA: benzyl bromide mixture led to a white precipitate whose structure corresponds to the salt as corroborated by ¹H-NMR (CDCl₃); thus, the methylene protons of the benzyl bromide shifted from 4.5 ppm to 4.8 ppm due to the formation of the salt (Figure S3).



Figure S4: ¹H NMR (400 MHz, CDCI₃) of the salt formed by mixing TEA and benzylbromide (20:1) at 4.8 (s, 2H) ppm.

Results and Discussion

2. Screening of the reaction conditions

the read					
		∕Br	CsPbBr₃ ►	~ ~	
		ED	, solvent, under N_2		
	1	λ = a	= 447 nm, (110 %)		46
Table S1	Results of th		20 II, 30°C	h perovskite C	sPbBr.
Entrv	Solvent	[ED] (equiv)	ICsPbBr₃1 (mol %)	Conv. (%)	Yield 3b (%)
1		TEA (20)	0.4	96	0
2		TEA (10)	0.4	85	ů 0
-		TEA (3)	0.4	36	0.2
4		TEA(20)	-	96	0
5		TEA (10)	_	87	0
6		TEA (3)	-	48	0
7		DIPEA (20)	0.4	22	22
8		DIPEA (10)	0.4	26	26
9	EtOAc	DIPEA (3)	0.4	37	38
10		DIPEA (20)	-	0	0
11		DIPEA (10)	-	0	0
12		DIPEA (3)	-	0	0
13		PPh ₃ (10)	0.4	88	4
14		PPh ₃ (3)	0.4	44	4
15		PPh ₃ (10)	-	69	0.1
16		$PPh_{3}(3)$	-	41	0
17		TEA (20)	0.4	80	0
18		TEA (10)	0.4	65	0
19		TEA (3)	0.4	64	31
20		TEA (20)	-	81	0
21		TEA (10)	-	66	0
22		TEA (3)	-	38	0
23		DIPEA (20)	0.4	45	42
24	T	DIPEA (10)	0.4	33	29
25	Toluene	DIPEA (3)	0.4	33	23
26		DIPEA (20)	-	0	0
27		DIPEA (10)	-	0	0
28		DIPEA (3)	-	0	0
29		PPh ₃ (10)	0.4	70	3
30		PPh ₃ (3)	0.4	48	4
31		PPh ₃ (10)	-	47	0
32		PPh ₃ (3)	-	15	0.2

Conditions: Catalyst CsPbBr₃ (0.004 mol%), Substrate 1a (34 mM), ED (TEA, DIPEA or PPh₃) in EtOAc (60 % v/v) or toluene (500 mL total reaction volume) irradiated at 447 nm for 20 h at 30 °C under N₂. The yields reported are GC-FID yields from at least two duplicates.

3. NMR of the isolated products from the studied reactions







Figure S7. $^{1}H^{-1}H$ COSY (CDCl₃, 500 MHz, 300 K) spectrum of the isolated product 2b.

---- 3.79

— 2.83

Figure S8: ¹H-NMR and ¹³C-NMR of product 3b.

Figure S10. 1 H- 1 H COSY (CDCl₃, 500 MHz, 300 K) spectrum of the isolated product 4b.

Figure S11. ¹H-NMR and ¹³C-NMR of product from entry 8, table .1

4. Electrochemical studies

Figure S14. CVs of the bare electrode (grey, a), benzyl bromide (2 mM, red, b) and benzyl bromide (2 mM) after the addition of DIPEA (10 eq) (green, c) in 0.1 M TBAPF₀/toluene /MeCN (85/15 V:V) electrolyte. The CV of benzyl bromide (red) shows an irreversible reduction peak at -2.15 V vs. SHE, which is slightly cathodically shifted (-2.19 vs SHE) upon addition of DIPEA.

Figure S15. CVs of the bare electrode (grey, **a**), benzyl bromide (2 mM, red, **b**) and benzyl bromide (2 mM) after the addition of TEA (10 equiv.) (green, **c**) and after the addition of TEA (10 equiv.) at a narrower window (purple, **d**) in 0.1 M TBAPF₆/toluene/MeCN (85/15 V:V) electrolyte. The CV of benzyl bromide (red) shows an irreversible reduction peak at -2.15 V vs. SHE, which is slightly cathodically shifted (-2.16 V vs SHE) upon addition of TEA.

Figure S16. CVs of the bare electrode (grey, a) and *p*-methoxybenzyl bromide (2 mM, red, b) in 0.1 M TBAPF₀/toluene /MeCN (85/15 V:V) electrolyte. The CV of *p*-methoxybenzyl bromide (red) shows an irreversible reduction peak at -2.05 V vs. SHE.

Figure S17. CVs of the bare electrode (grey, a) and *p-tert*-butylbenzyl bromide (2 mM, red, b) in 0.1 M TBAPF₀/toluene /MeCN (85/15 V:V) electrolyte. The CV of *p-tert*-butylbenzyl bromide (red) shows an irreversible reduction peak at -2.35 V vs. SHE.

Figure S18. CVs of the bare electrode (grey, a) and *p*-clorobenzyl bromide (2 mM, red, b) in 0.1 M TBAPF₆/ toluene /MeCN (85/15 V:V) electrolyte. The CV of *p*-clorobenzyl bromide (red) shows an irreversible reduction peak at -2.01 V vs. SHE.

Figure S19. CVs of the bare electrode (grey, a) and *p*-bromobenzyl bromide (2 mM, red, b) in 0.1 M TBAPF₆/toluene /MeCN (85/15 V:V) electrolyte. The CV of *p*-bromobenzyl bromide (red) shows an irreversible reduction peak at -2.14 V vs. SHE.

5. Computational studies

DFT calculations were carried out with the Gaussian09 program.⁴ The B3LYP exchange-correlation functional^{5, 6} was employed for geometry optimizations of the benzyl bromide derivative substrates (R = -OMe, -iBu, -H and -CI), with the standard 6-311+G* 6d basis set for C, N and H and the SDD pseudopotential for Cl and Br. The solvation effect of toluene was introduced through the SMD implicit solvent model.⁷ Dispersion effects were modeled with the Grimme-D₃ correction. The nature of stationary points was also established by frequency calculations in solvent-phase, where all minima have no imaginary frequencies.

Figure S20. DFT calculated redox potentials for the above showed redox processes: 1) One electron reduction and 2) dimerization of benzyl bromide derivatives. 3) one electron reduction of the derived radical of benzyl bromide derivatives. All the potentials are referred to SHE.

6. Analysis of the pre-concentration effect

The Nernst equation can be applied to estimate the equilibrium concentration of species in solution, and therefore the reaction rates. To clarify the effect of the redox difference between the photocatalyst (PC) and substrate (A) and the concentration of substrate in reaction rates, we have selected the following two cases.

In the first case, let us consider that the reaction is under homogeneous conditions, with half of a PC in the reduced form (PCⁿ⁻¹), and with a difference in redox potential ($\Delta E_{1/2}$) between PC and A of 0 V. Applying the Nernst equation [A]/[A-] = $e^{(\Delta E/(0.059 - ln([PC)/[PC-]))}$ to such conditions gives a relative concentration of reduced substrate (A-) vs the non-reduced substrate (A) of 50%. The relative reaction rate for a dimerization process of the reduced species A- can now be estimated. The reaction rate depends on the power of 2 with the concentration as follows d[P]/dt = k [A-]². Then, for an initial [A] concentration of 1 mM and a difference in redox potential between $E_{1/2}(PC)$ and $E_{1/2}(A)$ of 0 mV, in the steady-state, the [A-]/[A] ratio can be estimated as 1, [A-] = 5 + 10^{-4} M and the relative rate d[P]/dt = k + 2.5 + 10^{-7}, since the dimerization of radicals can be considered diffusion-controlled (k > 10⁸ M⁻¹ + s⁻¹), d[P]/dt = 25 M + s⁻¹.

In the second case, let us consider the same conditions, but the redox difference between $E_{1/2}(PC)$ and $E_{1/2}(A)$ is now modified to 650 mV, which is the redox difference expected between the conduction band edge energy of CsPbBr3 (-0.96 V vs SHE) and that of the benzyl bromide (-1.61 V vs SHE). Then, the effective concentration of A- is reduced to 0.002% and the reaction rate is d[P]/dt = $k \cdot 2.7 \cdot 10^{-16} = 2.7 \cdot 10^{-8} \text{ mM} \cdot \text{s}^{-1}$. Indeed, a redox difference of 650 mV has a dramatic effect on the dimerization rate. The same dramatic effect is valid for the concentration. For instance, maintaining the same conditions as in the second case, but with a local concentration of 1 M, the reaction rate is as fast as $2.7 \cdot 10^{-2} \text{ M} \cdot \text{s}^{-1}$. Therefore, substrate pre-concentration on a nanoparticle surface could increase the kinetics of the photocatalytic transformations.

∆E (mV)	[A] (M)	[A ⁻]/[A]	d[P]/d[t] (M·s⁻¹)
0	0.001	1	25
650	0.001	0.00002	2.7·10 ⁻⁸
650	0.01	0.00002	2.7·10 ⁻⁶
650	0.1	0.00002	2.7.10-4
650	1	0.00002	2.7·10 ⁻²

Table S2. Summary of the dependence of rate versus redox E_{1/2} and [A].

7. UV-vis spectroscopic studies

Figure S21. UV-Vis (*left*) and differential UV-vis (*right*) spectra of **CsPbBr**₃ (1.44 mM) in toluene (1 mL) at 298 K, before (**a**) and after (**b**) excitation at λ = 447 nm with a Blue LED, and (**c**) after the addition of benzyl bromide (1**a**, 35 mM) to **b** under irradiation (447 nm). Differential UV-vis spectra were obtained by subtraction of the initial CsPbBr₃ spectrum in the dark.

Figure S22. Differential UV-vis spectra (toluene 1 mL at 298 K) of an irradiated (447 nm) mixture containing *Left*) CsPbBr₃ (1.44 mM) and 1a (35 mM), a) before and b-g) after (0, 80, 100, 200, 300 and 400 s, respectively) the addition of Et₃N (0.35 M). *Right*) CsPbBr₃ (1 mM) and Et₃N (0.35 M) a-f) at different times after irradiation (0, 80, 100, 200, 300 and 400 s, respectively). Differential UV-vis spectra were obtained by subtraction of the initial spectrum of the mixture CsPbBr₃ and 1a (*Left*) and the initial CsPbBr₃ spectrum (*Right*), both in the dark.

Figure S23. Differential UV-vis spectra of CsPbBr₃ (1.44 mM) in toluene (1 mL) at 298 K, a) before and b) after 90 s from the addition of triethylamine (0.35 M), and c) after irradiation of b (447 nm). Differential UV-vis spectra were obtained by subtraction of the initial CsPbBr₃ spectrum in the dark.

8. Control studies

Figure S24: Absorption and emission spectra a) before and b) after the photocatalytic reaction and c) absorption and emission spectra of the resulting colloid perovskite, before and after the addition of increasing amounts of DDA (up to 70 µL). d) TEM images before and after the photocatalytic reaction and after the addition of 70 µL of DDA.

9. Characterization of homo- and hetero-coupling products

¹H-NMR (400 MHz, CDCl₃): δ = 7.33 - 7.26 (m, 4H), 7.23 - 7.17 (m, 6H), 2.93 (s, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 141.8 (2C), 128.5 (2C), 128.3 (2C), 125.9 (2C), 38.0 (2C) ppm. **MS** (EI): *m*/*z* 182.1 [M]. The spectroscopic characterization is in agreement with the literature reported.⁸

¹**H NMR** (400 MHz, CDCl₃): δ = 7.38 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 8.4 Hz, 4H), 2.84 (s, 4H). ppm. ¹³**C NMR** (101 MHz, CDCl₃) δ = 139.6 (2C), 131.8 (2C), 129.8 (2C), 128.5 (2C), 37.0 (2C) ppm. **MS** (EI): *m/z* 337.9 [M]. The spectroscopic characterization is in agreement with the literature reported.⁹

¹**H NMR** (400 MHz, CDCl₃): δ 7.08 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 3.79 (s, 4H), 2.83 (s, 4H) ppm. ¹³**C NMR** (101 MHz, CDCl₃) δ = 158.1 (2C), 134.33, (2C)129.7 (4C), 114.1(4C), 55.6 (2C), 37.6 (2) ppm. **MS** (EI): *m/z* 242.1 [M]. The spectroscopic characterization is in agreement with the literature reported.¹⁰

¹**H NMR** (400 MHz, CDCl₃): δ = 7.08 (d, J = 8.6 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 3.79 (s, 6H), 2.83 (s, 4H). ppm. ¹³**C NMR** (101 MHz, CDCl₃) δ = 157.8, 134.0, 129.7, 129.4, 113.8, 113.7, 55.3, 37.3 ppm. **MS** (EI): *m/z* 242.1 [M]. The spectroscopic characterization is in agreement with the literature reported.¹⁰

¹**H NMR** (400 MHz, CDCl₃): δ = 7.25 – 7.21 (m, 4H), 7.12 – 6.92 (m, 4H), 2.86 (s, 4H) ppm. ¹³**C NMR** (101 MHz, CDCl₃) δ = 139.6 (2C), 131.8 (2C), 129.8 (2C), 128.5 (2C), 37.0 (2C) ppm. **MS** (EI): *m*/*z* 182.1 [M]. The spectroscopic characterization is in agreement with the literature reported.¹¹

¹H NMR (400 MHz, CDCl₃): δ = 7.41 – 7.35 (m, 5H), 7.33 – 7.24 (m, 4H), 7.20 (dd, J = 7.8, 6.5 Hz, 3H), 7.17 – 7.13 (m, 2H), 7.01 (dd, J = 14.3, 8.4 Hz, 4H), 2.93 (s, 2H), 2.89 (s, 4H), 2.85 (s, 3H). ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 141.8, 141.2, 140.6, 140.1, 131.4, 131.3, 130.2, 128.4, 128.4, 128.4, 128.3, 126.04, 125.9, 119.8, 119.7, 37.9, 37.7, 37.3, 37.0.

¹**H** NMR (400 MHz, $CDCI_3$): δ = 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 7.12 – 7.04 (m, 2H), 6.84 – 6.80 (m, 2H), 3.79 (s, 3H), 2.91 – 2.85 (m, 4H) ppm. ¹³**C** NMR (101 MHz, $CDCI_3$) δ = 158.2, 142.2, 134.3, 129.7 (2C), 128.8 (2C), 128.7 (2C), 126.2, 114.1 (2C), 55.6, 38.6, 37.4 ppm. **MS** (EI): *m/z* 121.1 [M]. The spectroscopic characterization is in agreement with the literature reported.¹²

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