Supporting Information

Tailoring Heterojunction Energetics for High-Performance Self-Powered Halide Perovskite Photodetector Without Charge Transport Layers

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Experimental Procedures

Materials: Lead Bromide ($PbBr_2$, 99.9%, Sigma Aldrich), Cesium bromide (CsBr, 99.9%, Sigma Aldrich), Bismuth bromide ($BiBr_3$, 99.9%, Sigma Aldrich), Cesium carbonate (Cs_2CO_3, 99.9%, Sigma Aldrich) Silver bromide (AgBr, 99.9%, Sigma Aldrich), Oleylamine (OAM, .98%, Sigma Aldrich), Oleic Acid (OA, 90%, Sigma Aldrich), Dimethyl sulfoxide (DMSO, 90%, SRL), Octadecane (ODE, 90%, Sigma Aldrich), Hydrochloric acid (HCl, 35%) all chemicals were directly used without further purification.

Synthesis of Bi-CsPbBr$_3$ NCs:

Cs-oleate: Cs_2CO_3 (0.814 mg), OA (2.5 ml), and ODE (40 ml) were added into a three-neck flask and vacuum dried for 1 h at 120 ^0C. Subsequently, the reaction mixture was heated at 150 ^0C under N2 gas until the solution became transparent.

Synthesis of NCs: $PbBr_2$ (69 mg and 65.55 mg), $BiBr_3$ (0 mg and 4.22 mg), and 5 ml of ODE were added into a three-neck flask and vacuum dried at 120 ^0C for 1 h for undoped and Bi-doped CsPbBr$_3$ NCs. Subsequently, 0.5 ml of OA and 0.5 ml of Olam were injected into the mixture and dried at the same temperature, followed by heating to 185 ^0C under N_2 gas. At 185 ^0C, 0.4 ml of preheated Cs-oleate (~100 ^0C) was quickly injected into the reaction chamber. 5 seconds later, the mixture was cooled down in an ice-water bath. NCs were collected by centrifuging the crude solution by discarding the supernatant.
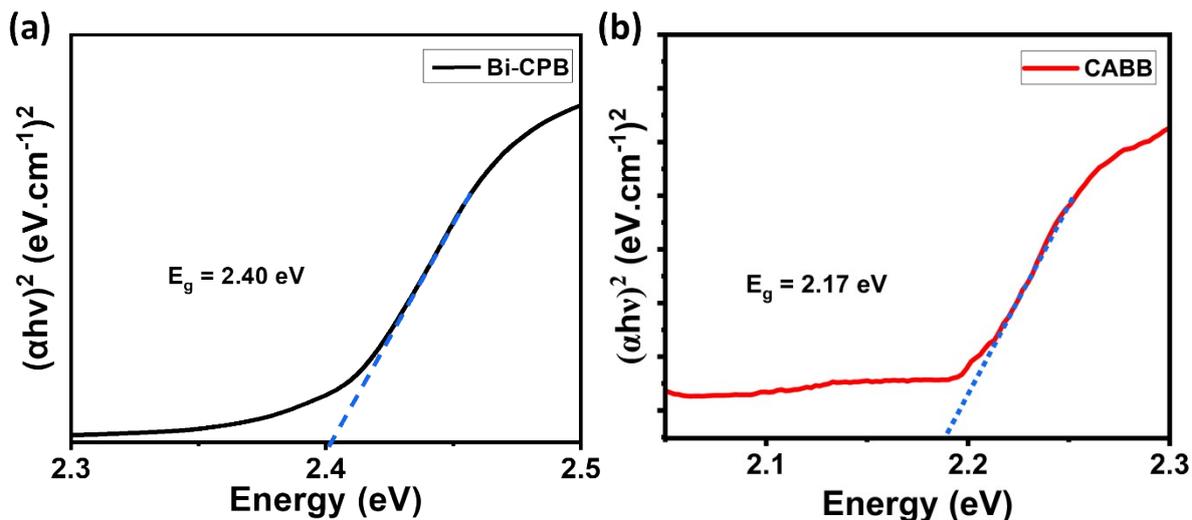
Figure S1. Tauc plot for (a) Bi-CPB, (b) CABB thin films for calculating bandgap energy (2.40 eV for Bi-CPB and 2.17 eV for CABB) of the material.
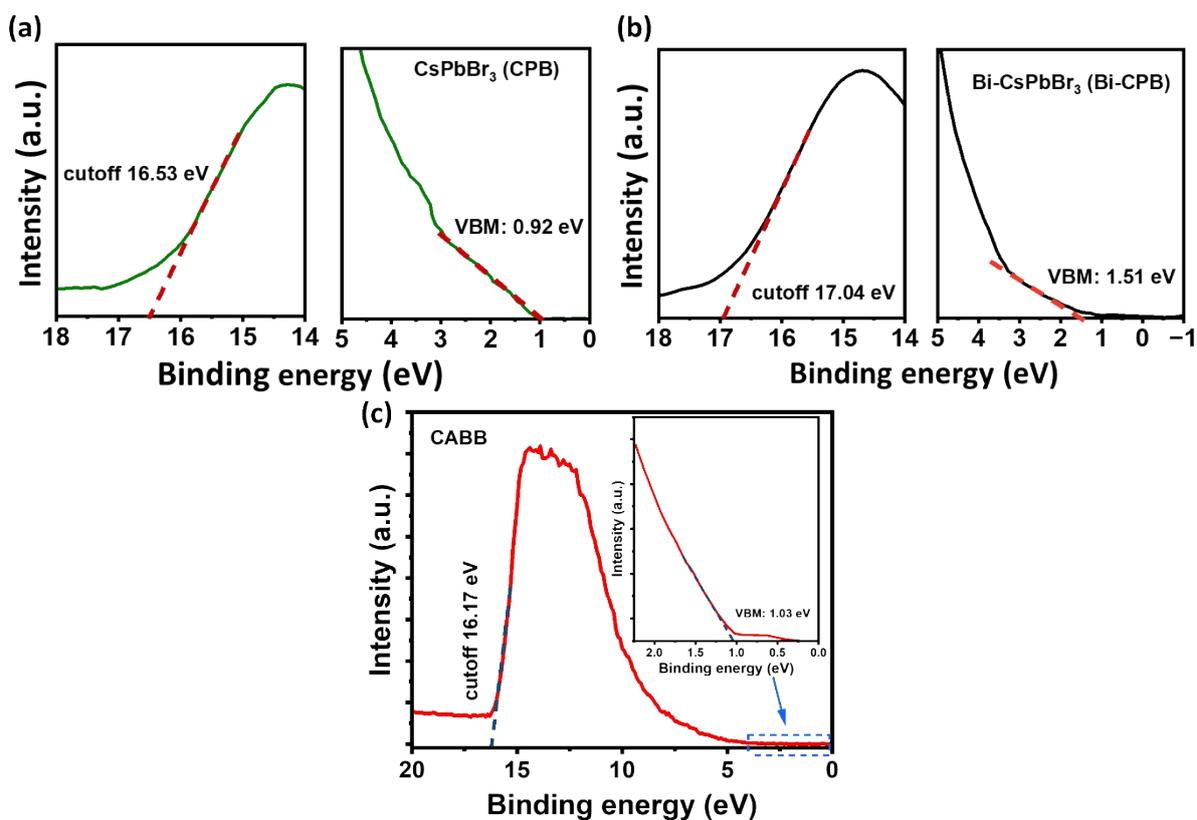

Figure S2. Ultraviolet photoelectron spectroscopy data for (a) $CsPbBr_3$, (b) Bi-$CsPbBr_3$ (Bi-CPB), and (c) CABB.

SI Note 1. <u>Analysis of UPS data:</u>

CsPbBr$_3$: Bandgap energy, E_g = 2.40 eV

Cut off energy = 16.53 eV

VBM position = 0.92 eV

Work function, W_f = $-$ (21.22 $-$ 16.53) = $-$ 4.69 eV

Valence band maxima, E_v = (W_f $-$ VBM) = ($-$ 4.69 $-$ 0.92) = $-$ 5.61 eV

Conduction band minima, E_c = E_g + E_v = (2.4 $-$ 5.61) = $-$ 3.21 eV

Bi-CsPbBr$_3$ (Bi-CPB): Bandgap energy, E_g = 2.40 eV

Cut off energy = 17.04 eV

VBM position = 1.51 eV

Work function, W_f = $-$ (21.22 $-$ 17.04) = $-$ 4.18 eV

Valence band maxima, E_v = (W_f $-$ VBM) = ($-$ 4.18 $-$ 1.51) = $-$ 5.69 eV

Conduction band minima, E_c = E_g + E_v = (2.4 $-$ 5.69) = $-$ 3.29 eV

Cs$_2$AgBiBr$_6$ (CABB): Bandgap energy, E_g = 2.17 eV

Cut off energy = 16.17 eV

VBM position = 1.03 eV

Work function, W_f = $-$ (21.22 $-$ 16.17) = $-$ 5.05 eV

Valence band maxima, E_v = (W_f $-$ VBM) = ($-$ 5.05 $-$ 1.03) = $-$ 6.08 eV

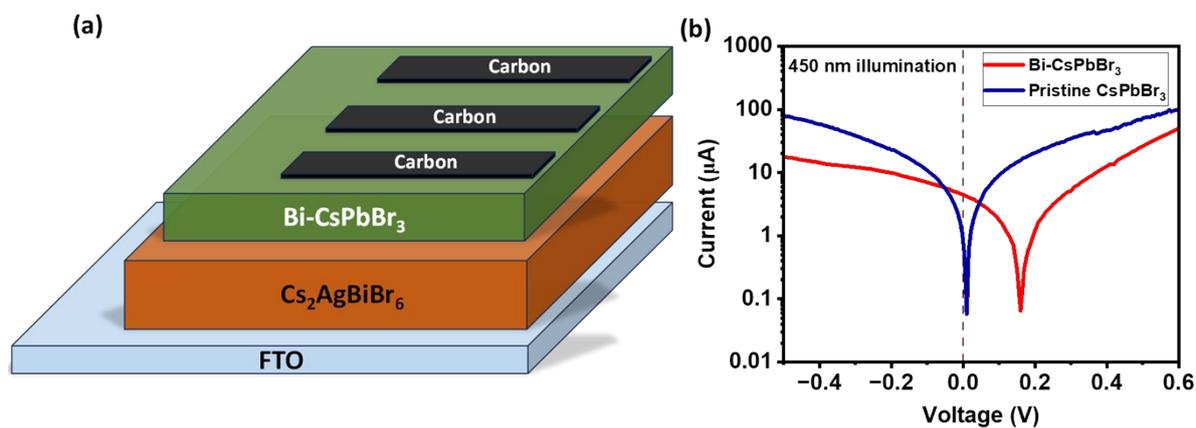Conduction band minima, E_c = E_g + E_v = (2.17 $-$ 6.08) = $-$ 3.91 eV

Figure S3. (a) Schematic diagram of a charge transfer layer (CTL) free photodetector based on FTO/CABB/Bi-CPB/Carbon. (b) Comparison of I-V characteristics for Bi-CsPbBr$_3$ (Bi-CPB) and Pristine CsPbBr$_3$ based CTL-free PDs under 450 nm illumination.
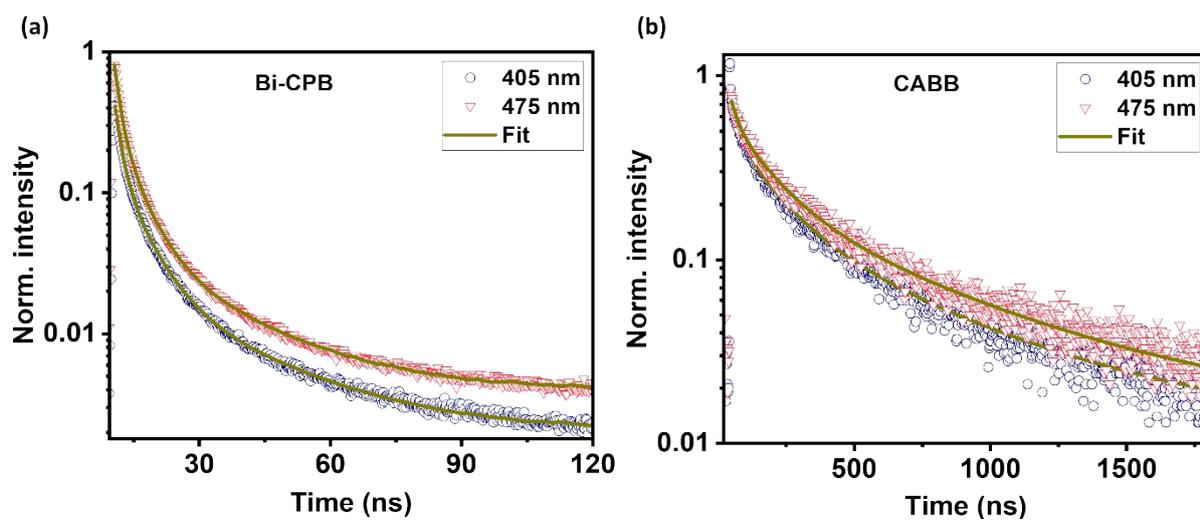

Figure S4. Comparison of TRPL data with 405 nm and 475 nm excitation for (a) Bi-CPB and (b) CABB, respectively.
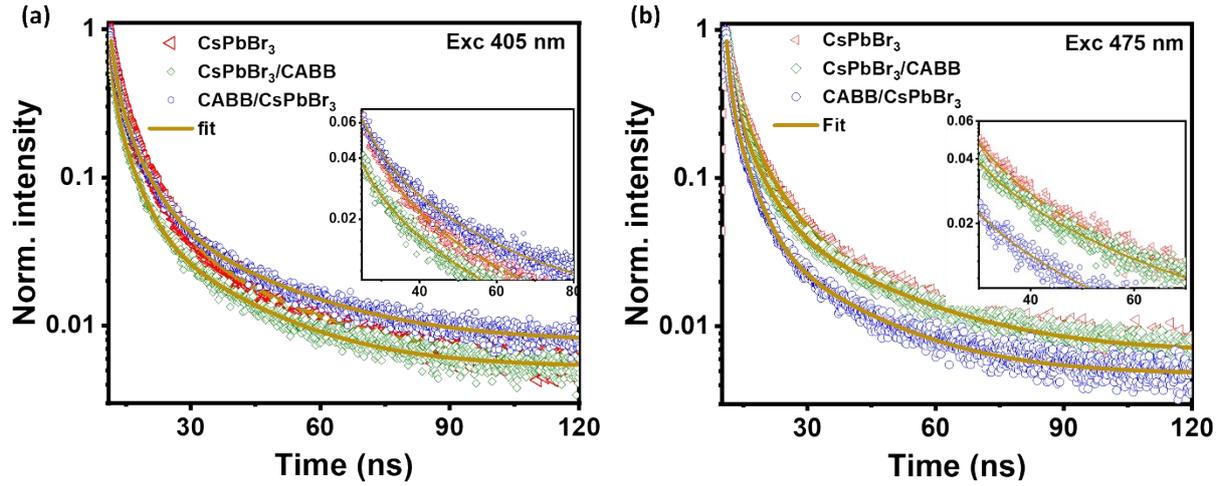
Figure S5. TRPL spectra of CsPbBr$_3$, CsPbBr$_3$/CABB, and CABB/CsPbBr$_3$ for (a) 405 nm excitation and (b) 475 nm excitation.

Table S1: TRPL fitting parameters for CsPbBr$_3$, CsPbBr$_3$/CABB, and CABB/CsPbBr$_3$ thin films with different excitation wavelengths

Excitation (nm)	Emission (nm)	Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	τ_{ave} (ns)
405	517	CsPbBr$_3$	1.65	20	5.2	51	22.5	29	9.5
		CsPbBr$_3$/CABB	0.89	21	3.9	45	19.1	34	8.4
		CABB/CsPbBr$_3$	1.30	17	5.0	44	23.0	39	11.0
475	517	CsPbBr$_3$	1.67	19	5.5	46	23.5	35	11.0
		CsPbBr$_3$/CABB	1.26	21	4.8	43	22.9	36	10.6
		CABB/CsPbBr$_3$	0.82	18	3.8	49	19.4	33	8.4

SI Note 2. Calculation of carrier mobility using the SCLC method:

In the space-charge-limited current (SCLC) method for extracting carrier mobilities, we have fabricated an electron-only device (FTO/TiO$_2$/Perovskite/PCBM/Carbon), and the dark I-V curves for Bi-CPB, CABB, and CABB/Bi-CPB-based devices are shown in **Figure S6**. Three distinct regions: ohmic (slope, n =1), trap-filled region (n >3), and trap-free region (n =2) were observed in the dark I-V curve. In the trap-free region, carrier mobility (μ) is calculated using the Mott-Gurney equation,[1, 2]

$$J = \frac{9}{8}\varepsilon_0\mu\varepsilon\frac{V^2}{L^3}$$

where J is the current density, ε is the dielectric constant, and L is the thickness of the active material. Calculated carrier mobility for Bi-CPB, CABB, and CABB/Bi-CPB are 7.8×10^{-4} cm^{2}s^{-1}V^{-1}, 1.2×10^{-4} cm^{2}s^{-1}V^{-1}, and 3.6×10^{-4} cm^{2}s^{-1}V^{-1}, respectively. These values are consistent with the previously reported results for similar material systems.[1, 3]
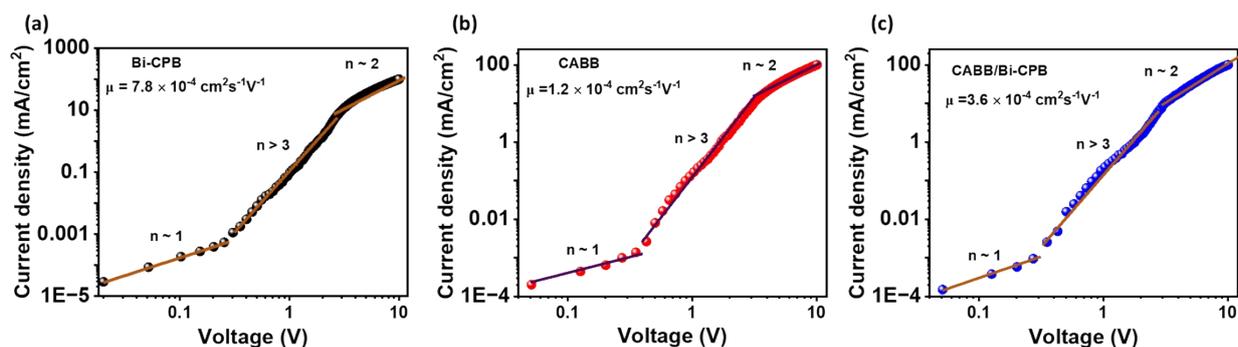
Figure S6. (a-c) Dark I-V plot for electron-only device (FTO/TiO$_2$/perovskite/PCBM/Carbon) for Bi-CPB, CABB, and Bi-CPB/CABB device, respectively.

References:

1. J. Luo, J. Xia, H. Yang, L. Chen, Z. Wan, F. Han, H. A. Malik, X. Zhu and C. Jia, *Energy & Environmental Science*, 2018, **11**, 2035-2045.
2. V. M. Le Corre, E. A. Duijnstee, O. El Tambouli, J. M. Ball, H. J. Snaith, J. Lim and L. J. A. Koster, *ACS energy letters*, 2021, **6**, 1087-1094.
3. X. Han, X. Wang, J. Feng, H. Huang, Z. Zhu, T. Yu, Z. Li and Z. Zou, *ACS Applied Electronic Materials*, 2020, **3**, 373-384.