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Supplementary Information

Polymer/Small-Molecule Binary-Blend Hole Transport Layer for Enhancing Charge Balance in Blue Perovskite Light Emitting Diodes

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Contents:

1. Experimental Details

1.1 Materials

1.2 Preparation perovskite precursor and blended HTLs

1.3 Fabrications of PeLEDs

1.4 Characterization

2. Figure S1 : UPS spectra perovskite.
3. Figure S2 : Photoluminescence quantum yield spectra of perovskite film.
4. Figure S3 : J-V characteristics of hole-only and electron only devices.
5. Figure S4. : Cross-sectional SEM images of PeLED device.
6. Figure S5 : Histogram of maximum EQE of devices based on various HTLs.
7. Figure S6 : EL spectra of PeLED under different biases.
8. Figure S7 : Operational stability test of the optimal PeLED.
9. Table S1 : PL decay profiles.
10. Table S2 : Summarized of blue (~ 480 nm) quasi-2D emissive PeLEDs parameters in the literature.

1. Experimental section

1.1 Materials

Indium tin oxide-based transparent conductive electrode (~4.5 Ω/sq ITO) was purchased from AMG. Poly(3,4-ethylenedioxythiophene): poly-styrene sulfonate (PEDOT:PSS, Clevios AI 4083) was purchased from Heraeus Clevios, poly (9-vinlycarbazole) (PVK, Mw=1, 100,000 g mol^{-1}), 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4oxadiazole) (PBD, ≥99%), lead bromide ($PbBr_2$, ≥98%), cesium bromide (CsBr, 99.999%), 2-pheneylethylamine hydrochloride (PEACl, ≥98%), yttrium (III) chloride (YCl_3, 99.99%), dimethyl sulfoxide (DMSO, 99.9%) and chlorobenzene (CB, 99.8%) were purchased from Sigma Aldrich. 2,2′,2″-(1,3,5-benzinetriyl) tris(1-phenyl-1-H-benzimidazole) (TPBi, 99.9%) was purchased from OSM and lithium fluoride (LiF, 99.9%) was obtained from iTASCO. All chemicals were used without further purification.

1.2 Preparation of Perovskite Precursor Solution and Blended HTLs

Perovskite: 45.9 mg $PbBr_2$ and 26.6 mg CsBr were dissolved in 0.5 mL DMSO, PEACl was dissolved in DMSO with a concentration of 1.2M and YCl_3 was dissolved in DMSO with a concentration of 0.25M. Then, 125 μL PEACl solution and 10 μL YCl_3 solution were added into the $CsPbBr_3$ precursor solution. The as-prepared was stirred at 60 °C and can be used after filtering with a 0.45 μm hydrophilic filter.

Blended HTLs: Dissolving PVK and PBD with different weight ratios (10:0, 9:1, 7:3, 5:5) in CB with the concentration of 4 mg mL^{-1}). The solution was spin-coated on PEDOT:PSS film at 4000 rpm for 40 s and the substrates were annealed at 120 °C for 10 minutes.

1.3 Device fabrication

The indium tin oxide (ITO) substrates were washed with detergent and deionized water, then sonicated in acetone and ethanol for 10 minutes, respectively. After drying in oven, the

substrates were treated with O_2 plasma cleaner for 10 minutes. PEDOT:PSS solution was spin coated on cleaned ITO at 4500 rpm for 40 s. After annealing at 140°C for 10 minutes, samples were transferred into glove box and HTLs were deposited on the PEDOT:PSS films. The perovskite precursor solution was spin-coated on HTL films at 500 rpm for 5 s and 5000 rpm for 40 s. After 15 s of spin-coating at 5000 rpm, 300 μL CB was dropped onto the substrate with above layers. After annealing at 100°C for 2.5 minutes, the samples were transferred to the thermal evaporation chamber, and TPBi (40 nm), LiF (1 nm) and Al (100 nm) were sequentially deposited at about 1×10^{-6} Torr by the thermal evaporation method. According to the area covered by the aluminum electrode, the defined area of the unit device is 0.135 cm^2.

1.4 Characterization

AFM was measured by a scanning probe microscope (Icon-PT-PLUS, RUKER). SEM was measured with Verios G4 UC (FEI) Smart Lab at the Hanyang LINC + Analytical Equipment Center (Seoul) with beam energy of 5kV. Steady-state PL measurements were carried out using a pulsed xenon lamp. Time-resolved PL decay measurements were carried out by a He-Cd laser operating at a wavelength of 375 nm. The $J-V-L$ characteristics, EQE and EL spectra were measured using a Konica Minolta spectroradiometer (CS-2000) with a Keithley 2400 source meter. Device characteristics were measured under ambient air conditions with encapsulation. UPS spectra were collected using a photoelectron spectrometer (Thermo Fisher Scientific Theta Probe) with a He I (21.22 eV) ultraviolet source in Smart Lab at the Hanyang LINC + analytical equipment center (Seoul). UV-Vis absorption spectra were measured by Varian Cary 5000 spectrophotometer. XRD patterns were measured using a using an X'Pert-MPD diffractometer (Philips, Netherlands) employing CuKα radiation. The GIWAXS results were observed using Xrays (E = 19.83 keV). PLQY measurement of the perovskite film was conducted with absolute photoluminescence quantum yields measurement system (Horiba Fluorolog3) equipped with an integrating hemisphere, and samples were excited at the

wavelength of 375 nm.

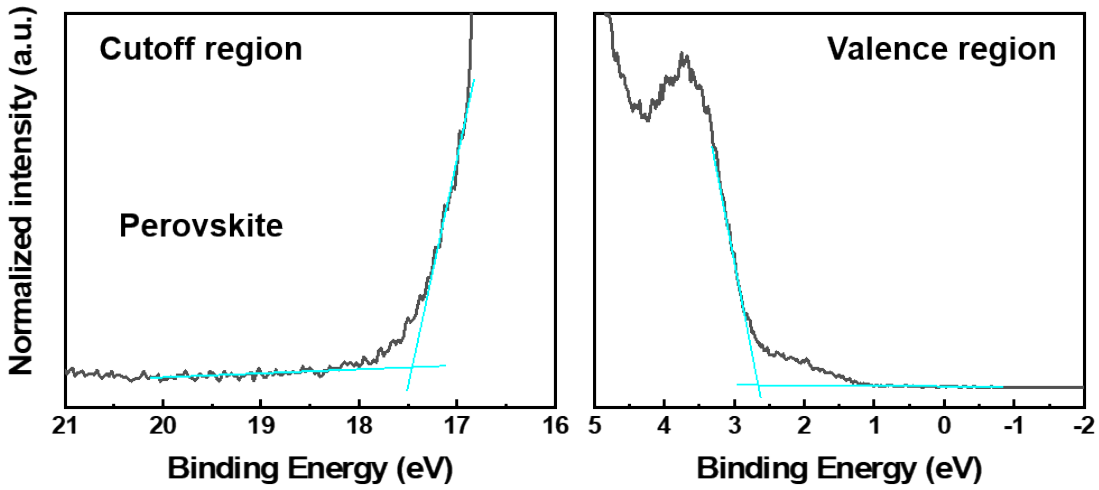

Figure S1. UPS spectra of $CsPbBr_3$:PEACl :YCl_3 perovskite.

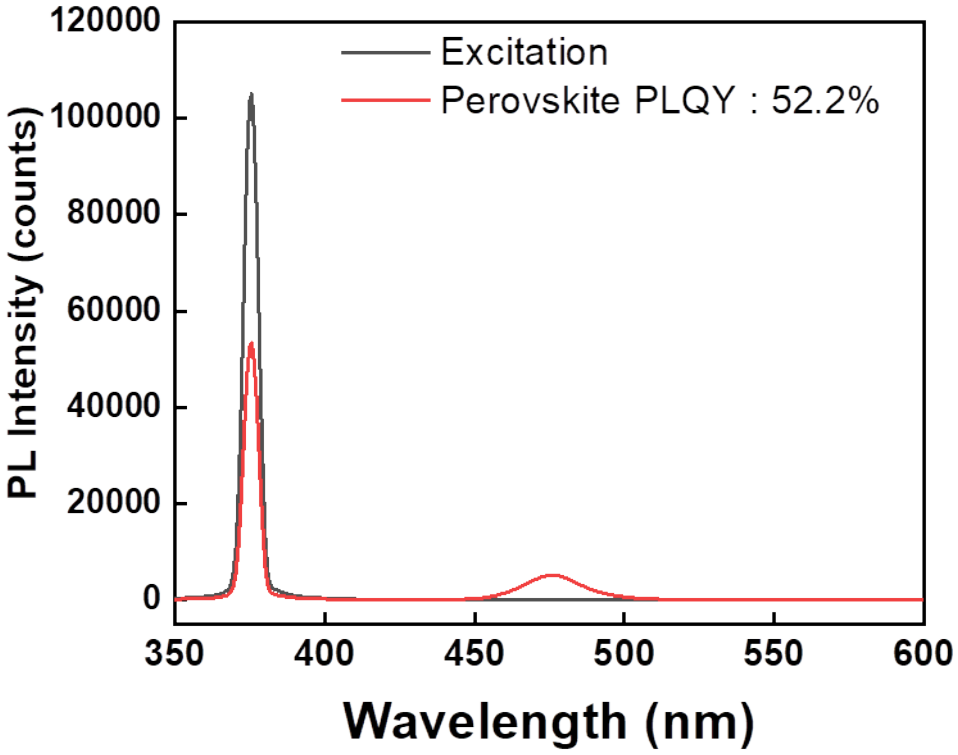

Figure S2. Photoluminescence quantum yield (PLQY) spectra of perovskite film.

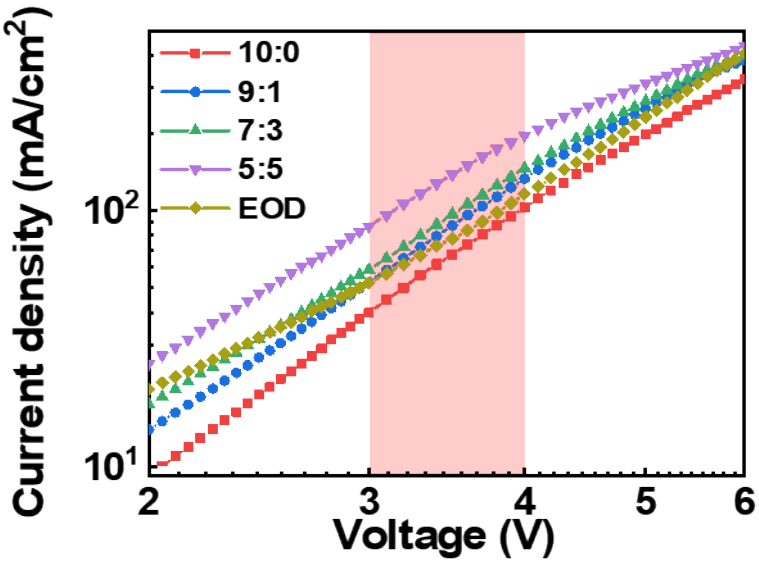

Figure S3. J-V characteristics of hole-only[a)] and electron only[b)] devices.
[a)]ITO/PEDOT:PSS/HTLs/Perovskite/MoO_3/Au
[b)]ITO/ZnO/Perovskite/TPBi/LiF:Al

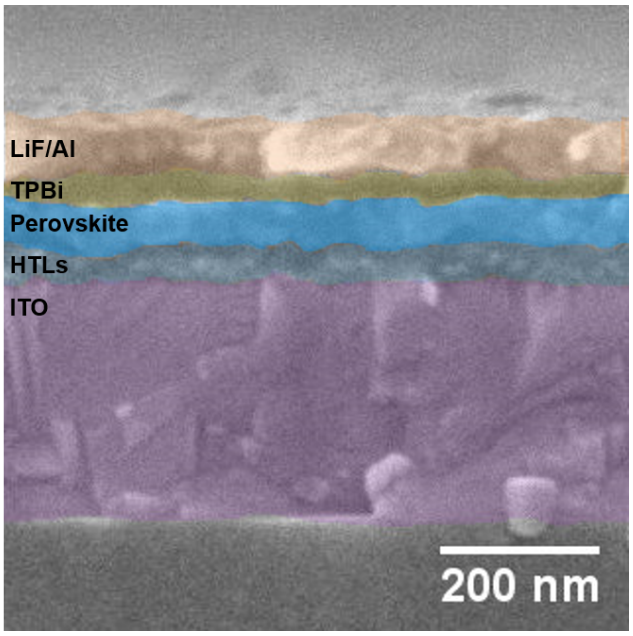

Figure S4. Cross-sectional scanning electron microscopy image of PeLED.

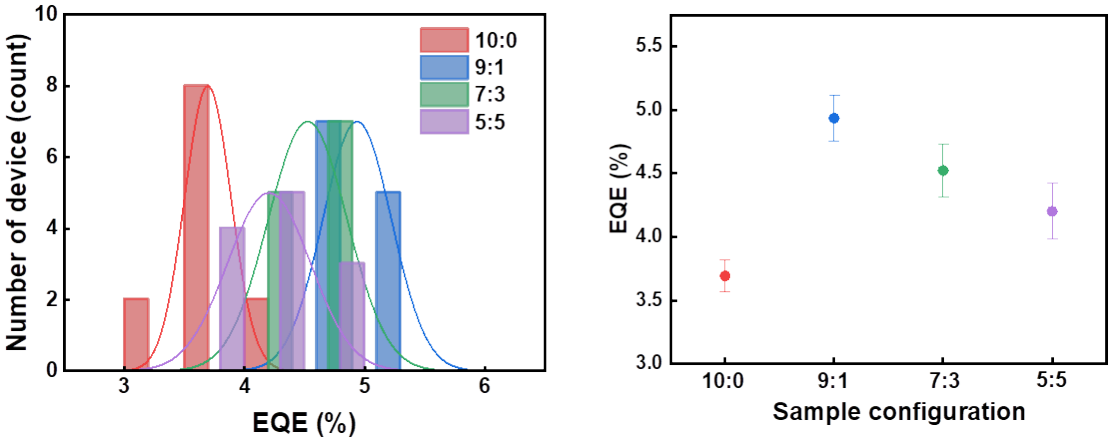

Figure S5. a) Comparison of EQE values for the devices with various HTLs. b) Histogram for the maximum EQE of devices based on various HTLs.

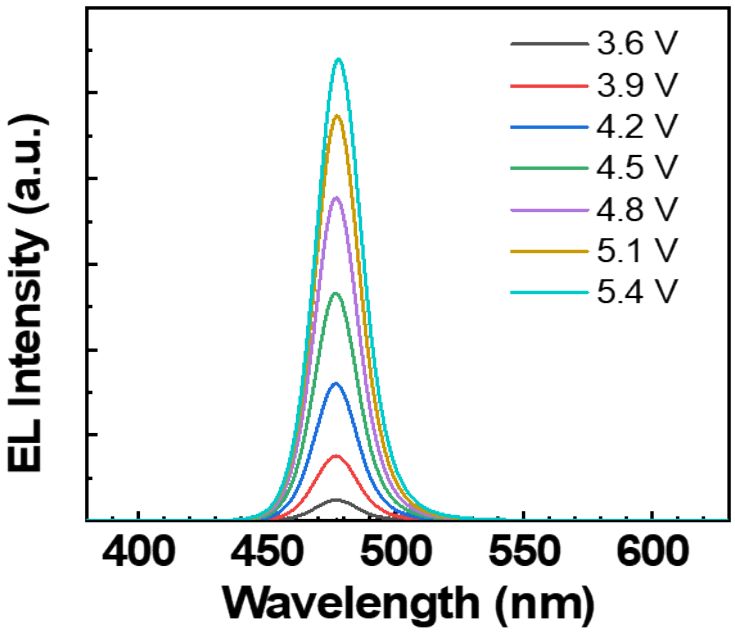

Figure S6. Electroluminesence spectra of PeLED under different biases.

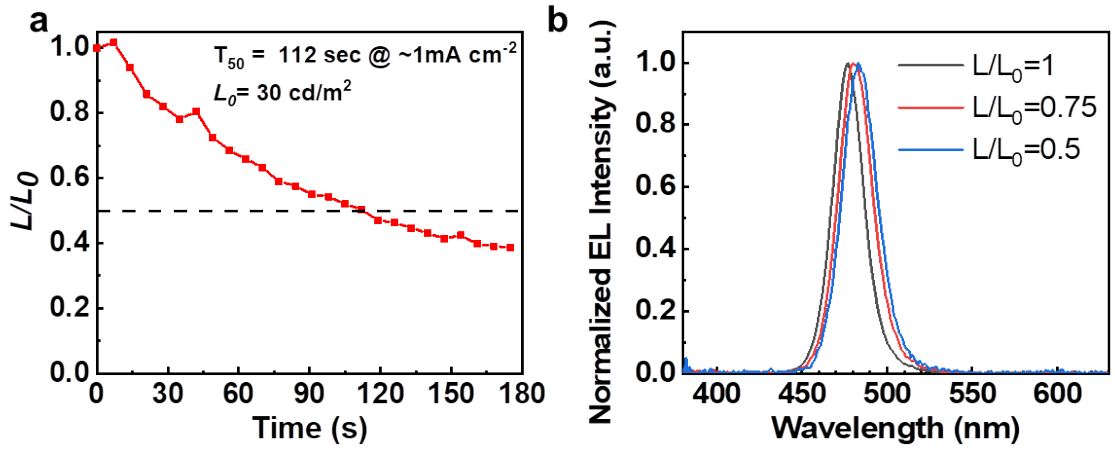

Figure S7. a) Operational stability test of the optimal PeLED. b) Electroluminescence spectra of each step.

Table S1. Time-resolved PL decay profiles of perovskite and with various HTLs films.

Sample configuration	**τ_1 (ns)**	**A_1 (%)**	**τ_2 (ns)**	**A_2 (%)**	**τ_3 (ns)**	**A_3 (%)**	**τ_{avg} (ns)**
Perovskite	57.98	4.08	11.07	29.90	2.65	66.92	7.35
PVK	41.24	4.97	8.45	29.41	2.11	65.62	5.92
PVK:PBD (9:1)	40.76	4.79	8.39	29.61	2.09	65.60	5.81
PVK:PBD (7:3)	41.48	4.06	8.03	29.35	1.79	66.59	5.23
PVK:PBD (5:5)	40.30	4.02	7.66	30.59	1.80	65.39	5.14

τ_1, τ_2, and τ_3: Lifetimes A_1, A_2 and A_3: Respective fractional contributions

τ_{avg}: Average lifetime (τ_{avg}) which is calculated using $\tau_{avg} = \sum_{i=1}^{3} Ai \cdot \tau i$

Table S2. Summarized of blue (~ 480 nm) quasi-2D emissive PeLEDs parameters in the literature.

Perovskite	Emission peak [nm]	EQE_{max} [%]	L_{max} [cd/m^2]	CE_{max} [cd/A]	Reference
[1]$PEA_2(Cs_{1-x}EA_xPbBr_3)_2PbBr_4$	480	4.19	83	6.17	Nat. Commun. **2020** 11, 4165
[1]$CsPbCl_{0.9}Br_{2.1}$:PEABr	480	5.7	3780	6.1	Nat. Commun. **2019** 10, 1027
[1]$PEA_2Cs_{1.6}MA_{0.4}Pb_3Br_{10}$	479	5.2	468	-	J. Am. Chem. Soc. **2020** 142, 5126
[2]$CsPbBr_3$:GABA	478	6.3	200	-	Nat. Commun. **2020** 11, 3674
[3]MePEABr:$CsPbBr_3$	477	2.9	154	2.6	Adv. Funct. Mater. **2021** 31, 2103299
[1]PEA-$Rb_{0.3}Cs_{0.7}PbBr_{2.7}Cl_{0.3}$	475	10.1	14000	-	Adv. Mater. **2021** 33, 2100783
[4]NEA-$FAPbBr_{3-x}Cl_x$	474	3.1	2810	-	Nano Energy **2021** 79, 105486
[5](Cs/FA/p-F-PEA)$Pb(Cl/Br)_3$	469	4.14	451	2.71	Adv. Funct. Mater. **2020** 2006736
[6](Rb/Cs/FA)$Pb(Cl/Br)_3$:TTDDA	467	5.5	200~	-	Nat. Commun. **2021** 12, 361
[7]PBABr:(Cs/FA/MA)$PbBr_3$	465	2.34	144.9	-	ACS Energy Lett. **2020** 5, 1593
[1]$CsPbBr_3$:PEACl :YCl_3	478	5.30	167	4.42	**Our work**

[1]PEA: phenylethylammonium, [2]GABA: γ-aminobutyric acid, [3]MePEA: methoxy phenethylammonium,
[4]NEA: 2-(2-naphthyl)ethanamine, [5]p-F-PEA: 4-Fluorophenylethylammonium,
[6]TTDDA: 4,7,10-trioxa-1,13-tridecanediamin, [7]PBA: 4-Phenylbutylammonium.