Supporting information

Orthogonal Lithography for Halide Perovskite Optoelectronic Nanodevices

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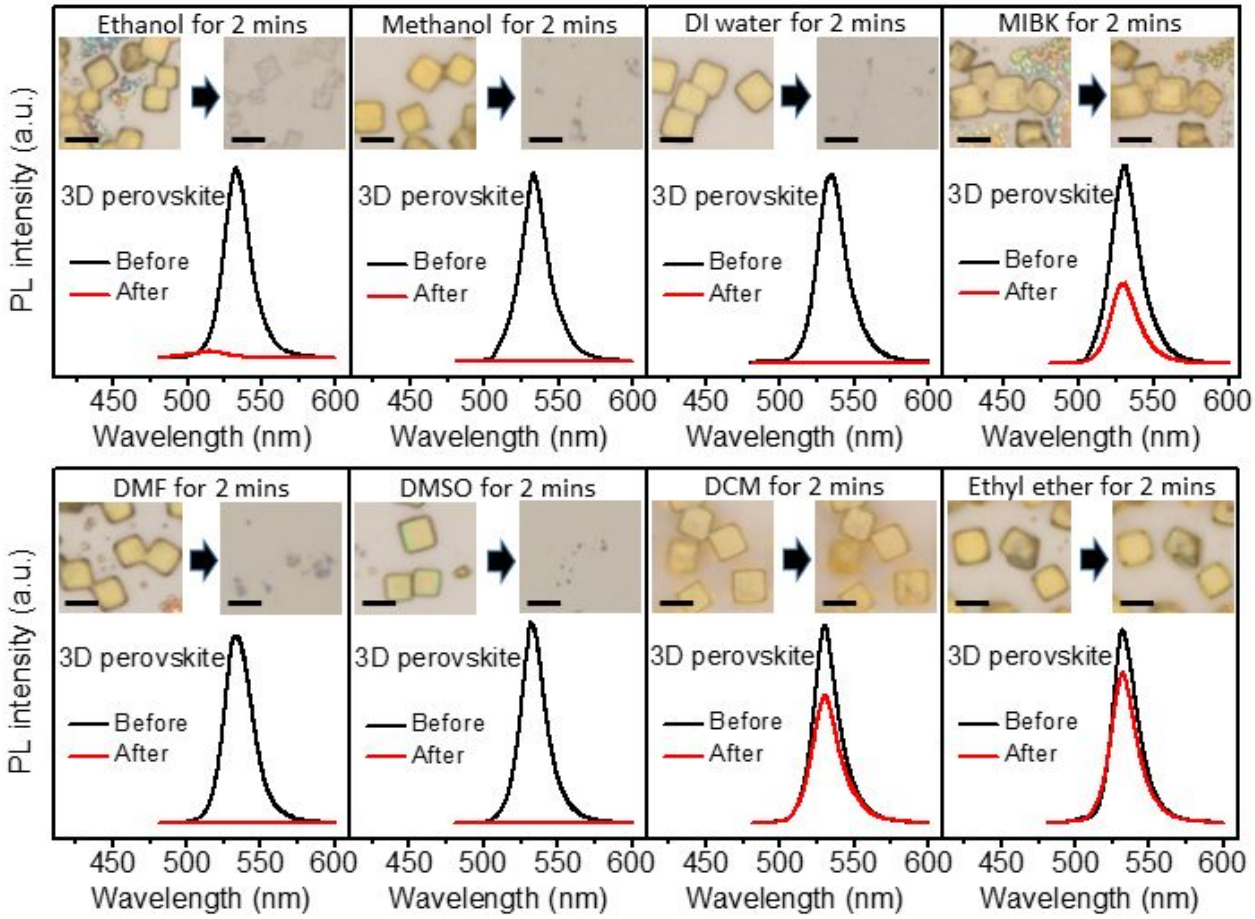

Figure S1. Solvent orthogonality tests on the 3D $CH_3NH_3PbBr_3$ perovskite. The PL spectra and optical images of the 3D $CH_3NH_3PbBr_3$ crystals before and after immersion in ethanol, methanol, deionized (DI) water, methyl isobutyl ketone (MIBK), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), dichloromethane (DCM), and ethyl ether for 2 min. The length of the scale bars is 10 μm.

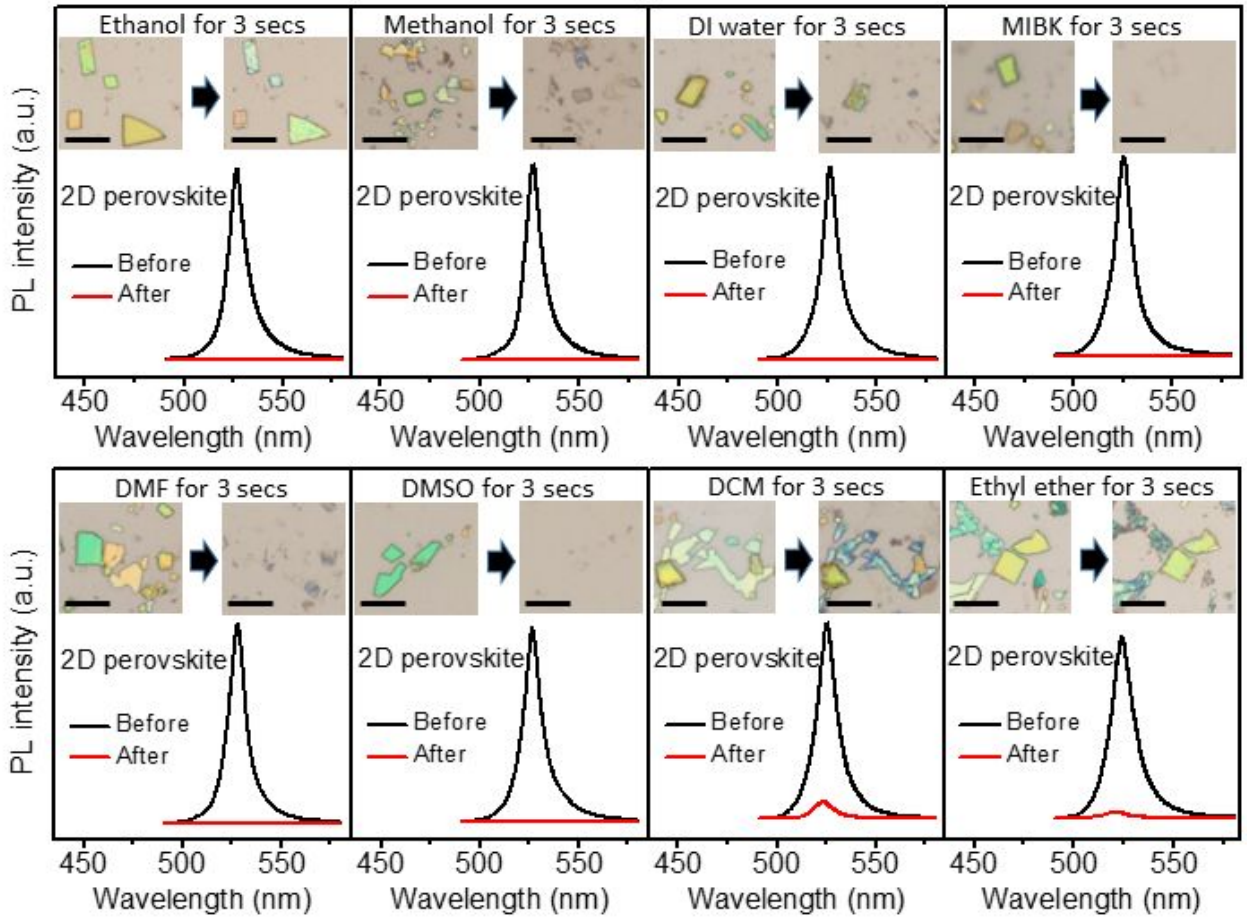

Figure S2. Solvent orthogonality tests on the 2D $(C_6H_5C_2H_4NH_3)_2PbI_4$ perovskite. The PL spectra and optical images of the 2D $(C_6H_5C_2H_4NH_3)_2PbI_4$ crystals before and after immersion in ethanol, methanol, deionized (DI) water, methyl isobutyl ketone (MIBK), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), dichloromethane (DCM), and ethyl ether for 3 s. The length of the scale bars is 10 μm.

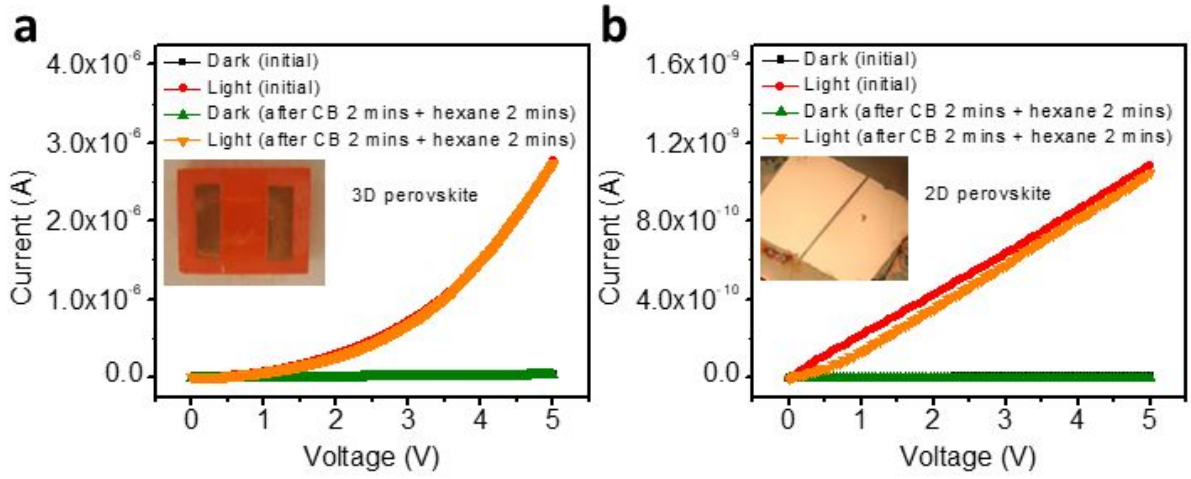

Figure S3. The electrical properties of the 3D and 2D perovskite devices before and after sequential treatments by hexane and chlorobenzene (CB) for 2 min each. Au electrodes were deposited on the 3D and 2D mm-scale single crystals using an e-beam evaporator. We then measured the *I-V* characteristics of (a) 3D and (b) 2D devices in the dark and under AM 1.5G solar light before and after sequential treatments by hexane and chlorobenzene for 2 min each. The photocurrent and dark current showed no significant change after these treatments for either sample, indicating the excellent chemical orthogonality of hexane and chlorobenzene to the perovskites.

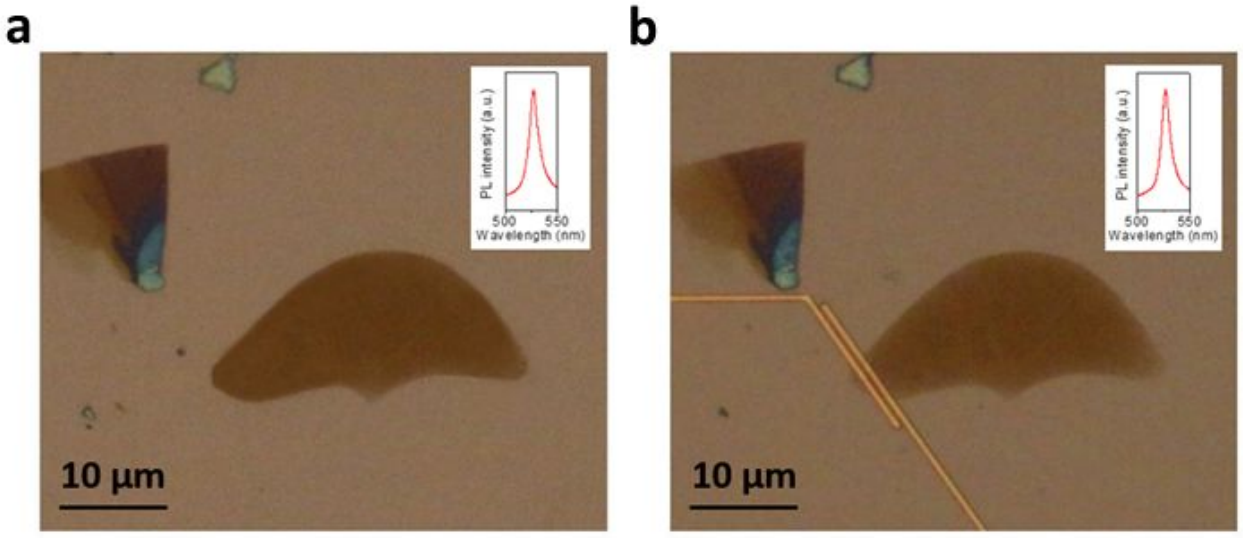

Figure S4. Optical microscope images of the 2D perovskite sample (a) before and (b) after the orthogonal EBL fabrication. The insets are the PL spectrum of the 2D perovskite for both cases.

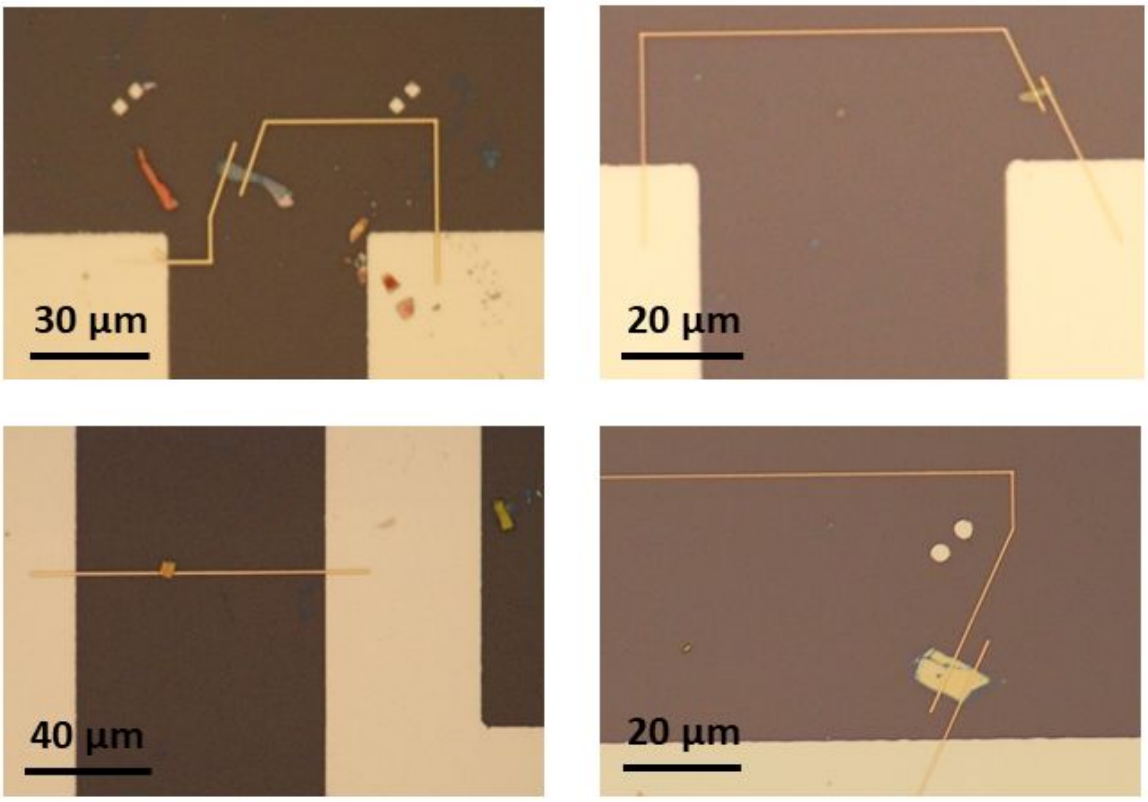

Figure S5. Four other devices were fabricated on 2D $(C_6H_5C_2H_4NH_3)_2PbI_4$ perovskite single crystals, featuring various patterned electrodes using the orthogonal EBL method to demonstrate the reliability and reproducibility of this technique.

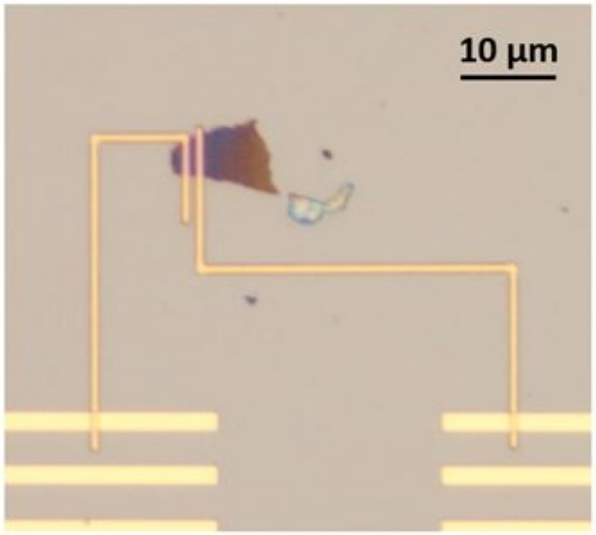

Figure S6. A 2D $(HOC_2H_4NH_3)_2PbI_4$ device was fabricated to demonstrate that the proposed orthogonal EBL method is also suitable for different kinds of perovskites.

Table S1. Single crystal XRD data and structure refinement of $CH_3NH_3PbBr_3$.

Empirical formula	Br_3 Pb
Formula weight	446.90
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	P m -3 m
Unit cell dimensions	
a = 5.9199(2) Å	$\alpha = 90°$
b = 5.9199(2) Å	$\beta = 90°$
c = 5.9199(2) Å	$\gamma = 90°$
Volume	207.46(2) $Å^3$
Z	1
Density (calculated)	3.577 Mg/m^3
Absorption coefficient	34.657 mm^{-1}
F(000)	187
Crystal size	0.10 x 0.10 x 0.08 mm^3
Theta range for data collection	3.441° to 26.175°
Index ranges	-7<=h<=6, -7<=k<=7, -7<=l<=7
Reflections collected	1472
Independent reflections	68 [R(int) = 0.1545]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9484 and 0.1482
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	68 / 0 / 5
Goodness-of-fit on F^2	1.413
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1343
R indices (all data)	R1 = 0.0441, wR2 = 0.1343
Extinction coefficient	0.10(2)

Largest diff. peak and hole	1.748 and -1.430 e. $Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic atomic displacement parameters ($Å^2$ x 10^3) for $CH_3NH_3PbBr_3$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	**y**	**z**	**U(eq)**
Pb(1)	0	0	0	32(2)
Br(1)	5000	0	0	104(3)

Table S3. Single crystal XRD data and structure refinement of $(C_6H_5C_2H_4NH_3)_2PbI_4$.

Empirical formula	C_{16} H_{24} I_4 N_2 Pb
Formula weight	959.16
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	
a = 8.6879(4) Å	α = 94.496(2)°
b = 8.6903(5) Å	β = 100.523(2)°
c = 16.4242(8) Å	γ = 90.568(2)°
Volume	1215.06(11) $Å^3$
Z	2
Density (calculated)	2.622 Mg/m^3
Absorption coefficient	12.025 mm^{-1}
F(000)	856
Crystal size	0.10 x 0.08 x 0.02 mm^3
Theta range for data collection	1.265 to 26.419°
Index ranges	-10<=h<=8, -10<=k<=10, -20<=l<=20
Reflections collected	20297
Independent reflections	4987 [R(int) = 0.0354]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.80 and 0.43
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4987 / 210 / 354
Goodness-of-fit on F^2	1.295
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0889
R indices (all data)	R1 = 0.0327, wR2 = 0.0987
Extinction coefficient	n/a

Largest diff. peak and hole	1.285 and -2.063 e. $Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic atomic displacement parameters ($Å^2$ x 10^3) for $(C_6H_5C_2H_4NH_3)_2PbI_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pb(1)	5000	5000	5000	9(1)
Pb(2)	0	0	5000	9(1)
I(1)	5814(1)	5325(1)	6992(1)	20(1)
I(2)	3135(1)	1876(1)	5020(1)	12(1)
I(2A)	1872(7)	3124(7)	4983(4)	30(2)
I(3)	-670(1)	-180(1)	3010(1)	20(1)
I(4)	-1893(1)	3108(1)	5000(1)	12(1)
I(4A)	-3097(8)	1892(7)	5000(4)	32(2)
N(1)	9769(8)	6045(8)	6627(4)	25(1)
C(1)	10982(10)	5004(9)	6985(5)	24(2)
C(2)	10860(20)	4730(20)	7889(11)	28(3)
C(2A)	11730(20)	5590(20)	7905(11)	29(3)
C(3)	11160(20)	6230(20)	8441(10)	21(3)
C(3A)	10506(19)	5550(20)	8440(10)	20(3)
C(4)	12680(20)	6851(19)	8669(10)	24(3)
C(4A)	9958(19)	4170(20)	8654(10)	23(3)
C(5)	13000(20)	8240(20)	9168(11)	31(3)
C(5A)	8840(20)	4160(30)	9143(12)	37(4)
C(6)	11720(20)	9040(20)	9407(11)	35(3)
C(6A)	8180(20)	5490(30)	9400(11)	38(4)
C(7)	10240(20)	8440(20)	9167(10)	32(3)
C(7A)	8710(20)	6860(30)	9182(12)	39(4)
C(8)	9903(11)	6997(11)	8691(5)	32(2)
N(2)	6352(16)	1042(15)	6634(9)	20(3)

N(3)	4777(15)	-556(15)	6633(8)	19(3)
C(9)	5490(20)	-120(20)	7006(11)	26(4)
C(9A)	6100(20)	530(20)	7012(10)	23(3)
C(10)	6180(30)	-260(20)	7912(11)	25(3)
C(10A)	6720(20)	320(30)	7917(11)	25(3)
C(11)	6200(20)	1217(19)	8441(10)	20(3)
C(11A)	5480(18)	511(19)	8439(9)	16(2)
C(12)	7650(20)	2030(20)	8765(10)	26(3)
C(12A)	4876(19)	-790(20)	8768(10)	24(3)
C(13)	7620(30)	3440(20)	9242(11)	36(4)
C(13A)	3700(20)	-580(20)	9252(13)	38(4)
C(14)	6270(30)	4040(20)	9400(11)	39(4)
C(14A)	3160(20)	850(20)	9387(10)	34(4)
C(15)	4830(30)	3260(20)	9091(11)	34(4)
C(15A)	3690(20)	2150(20)	9072(10)	28(3)
C(16)	4869(10)	1896(10)	8622(5)	25(2)