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Supporting Information

Two-Dimensional Organic-Inorganic Hybrid Perovskite Field-Effect Transistors with Polymers as Bottom-Gate Dielectrics

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Experimental section

Materials.

Poly(vinyl alcohol) (PVA, molecular weight, 85000-124000), poly(4-vinylphenol) (PVP, molecular weight, 25000), 4,4-(hexafluoroisopropylidene) diphthalic anhydride (HAD, >99%), triethylamine (TEA, >99%) and propylene glycol monomethyl ether acetate (PGMEA, >99.5%) were purchased from Sigma-Aldrich. Tin(Ⅱ) iodide (SnI_2, 99.9%) and N,N-dimethylmethanamide (DMF, 99.8%) were supplied by Alfa Aesar. Phenylethylammonium iodide (PEAI, 99%) was bought from Xi'an Polymer Light Technology Corp. All materials were used as received without further purification.

Gate dielectric layer preparation.

The gate dielectric layers of PVA modified by cross-linking PVP (CL-PVP) were prepared on indium tin oxide (ITO)-coated glass substrates with a sheet resistivity of 15 Ω sq^{-1}. The substrates were first cleaned with diluted detergent, successively ultrasonicated in deionized water, acetone, and ethyl alcohol for 30 min each, and then dried with nitrogen gas. The substrates were treated with UV-ozone for 20 min before dielectric film deposition. PVA was dissolved in deionized water at a concentration of 60 mg ml^{-1} and stirred and heated at 80 ℃ for 1 h before use. Then, the PVA films were spin coated on the precleaned substrates from the water solution at 3000 rpm for 40 s and annealed at 60 ℃ for 12 h in a vacuum oven. A standard PVP solution with HDA as a cross-linking agent at a weight ratio of 10:1 (PVP:HDA) was prepared in PGMEA at a concentration of 20 mg ml^{-1}. TEA with a catalytic amount of 3% based on the number of PVP monomers was added in the standard PVP solution and the solution was shaken overnight according to the literature.[1,2] The CL-PVP films were spin coated on the PVA layers at 1500 rpm for 40 s and then annealed at 200℃ for 1 h in vacuum to promote the cross-linking reaction, forming modifying layers on PVA.

Active layer preparation.

The $(PEA)_2SnI_4$ thin films were prepared according to a previous report.[3] PEAI and SnI_2 at a stoichiometric molar ratio of 2:1 were dissolved in DMF and stored for 2 h to form a perovskite precursor solution. The precursor solution with a concentration of 0.3 M was spin coated on the polymer gate dielectric layer at 4000 rpm for 30 s and annealed at 100 °C for 15 min on a hot plate in nitrogen.

Device fabrication.

Finally, an 80-nm Au layer was thermally deposited on the top of the perovskite film with a shadow mask under vacuum of 5×10^{-6}Torr, serving as the source and drain electrode. The length and width of the channel in the $(PEA)_2SnI_4$ field-effect transistor (FET) are 50 and 1000 μm, respectively. The sandwiched polymer dielectric devices for capacitance and leakage current measurements and the lateral and vertical $(PEA)_2SnI_4$ devices for investigating charge carrier injection and transport were fabricated based on the abovementioned fabrication procedures accordingly.

Characterizations.

The morphologies of the films were characterized by scanning electron microscopy (SEM, Hitachi S-4800), atomic force microscopy (AFM, Shimadzu SPM-9700), and an optical microscope. The thickness of the layer in the layered $(PEA)_2SnI_4$ thin film was determined by AFM as well. The X-ray diffraction (XRD) patterns of the as-prepared $(PEA)_2SnI_4$ films on glass substrates were recorded by a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å, 40 kV, 40 mA). The ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra were measured by a Shimadzu UV-3101PC spectrophotometer and a Fluorolog (Horiba) spectrofluorometer, respectively. UV photoelectron spectroscopy (UPS) images were taken on a Kratos Axis Ultra DLD spectrometer with He (I) UV light (21.22 eV) as an excitation source and a bias voltage of -9 V under high vacuum (3.0×10^{-8} Torr). The water and CH_2I_2 contact angles were measured using a contact angle system (XYCXIEXG-CAM) and surface energies were calculated from the contact angles by the Owens-Wendt-Rabel-Kaelble method. The currents of the dielectric layers and the

active layers and the output and transfer characteristics of the $(PEA)_2SnI_4$ transistors were measured with a Keithley 4200 semiconductor analyzer. The capacitance-voltage measurements of the dielectric layers and the transistors were conducted on an Agilent E4990A impedance analyzer with a small superimposed AC signal of 100 mV at 100 kHz. All measurements were performed at room temperature in air.

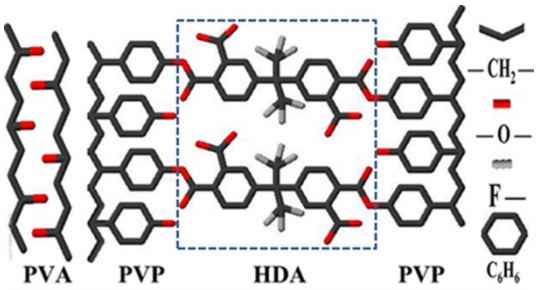

Figure S1. Molecular structures of PVA and cross-linking PVP with HDA as a cross-linking agent.

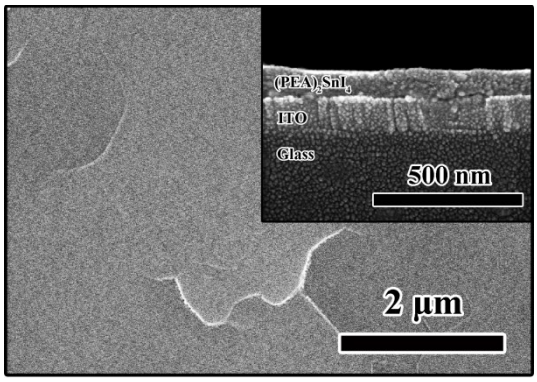

Figure S2. SEM image of the $(PEA)_2SnI_4$ thin film deposited on an ITO-glass substrate. The inset exhibits the cross-sectional SEM image of the film.

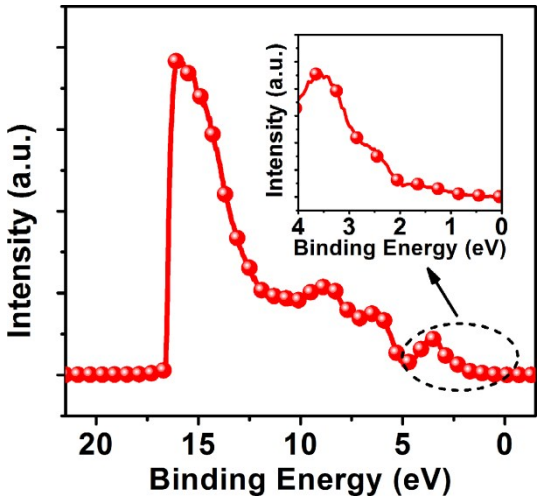

Figure S3. UPS spectrum of the $(PEA)_2SnI_4$ thin film on an ITO-glass substrate.

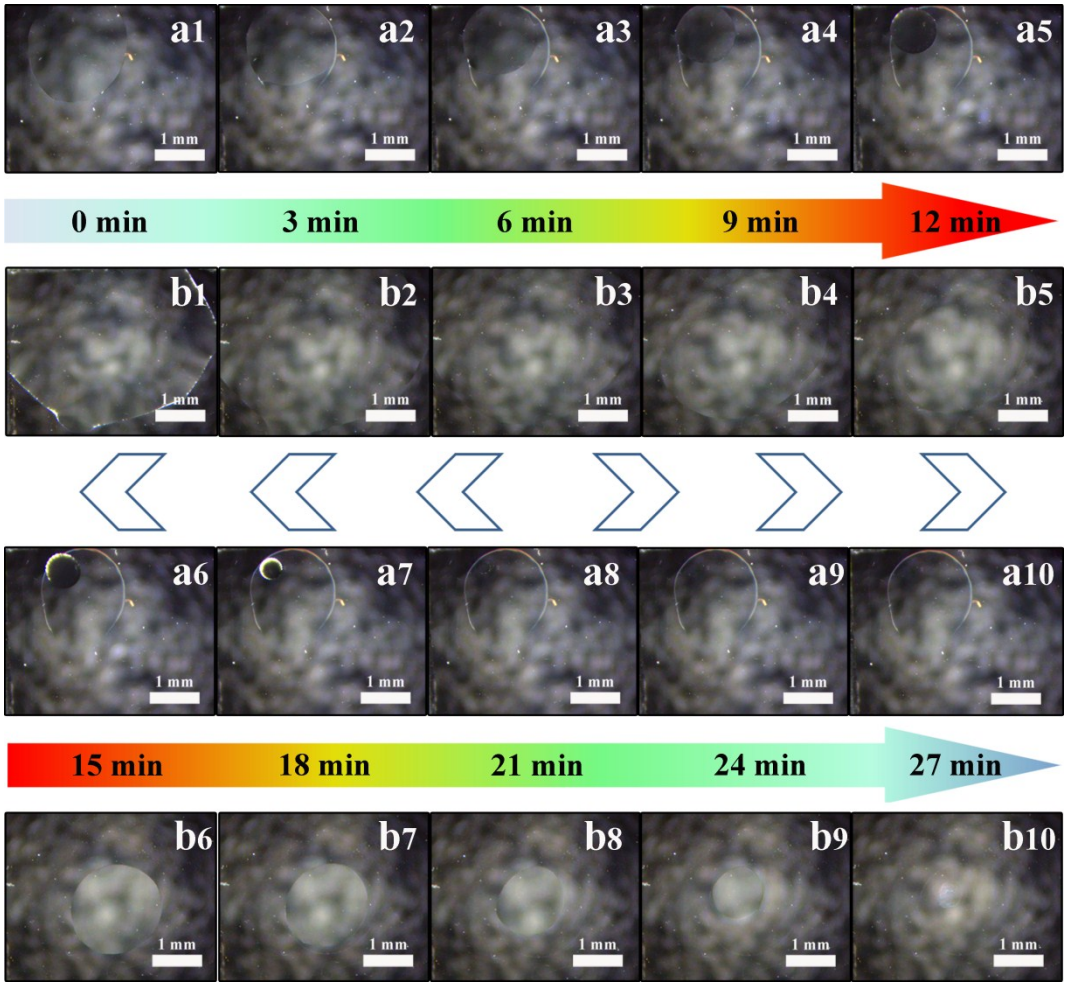

Figure S4. Optical microscope images of the PVA (a1-a10) and PVA/CL-PVP (b1-b10) films treated with DMF drops, exhibiting their surface changes over time.

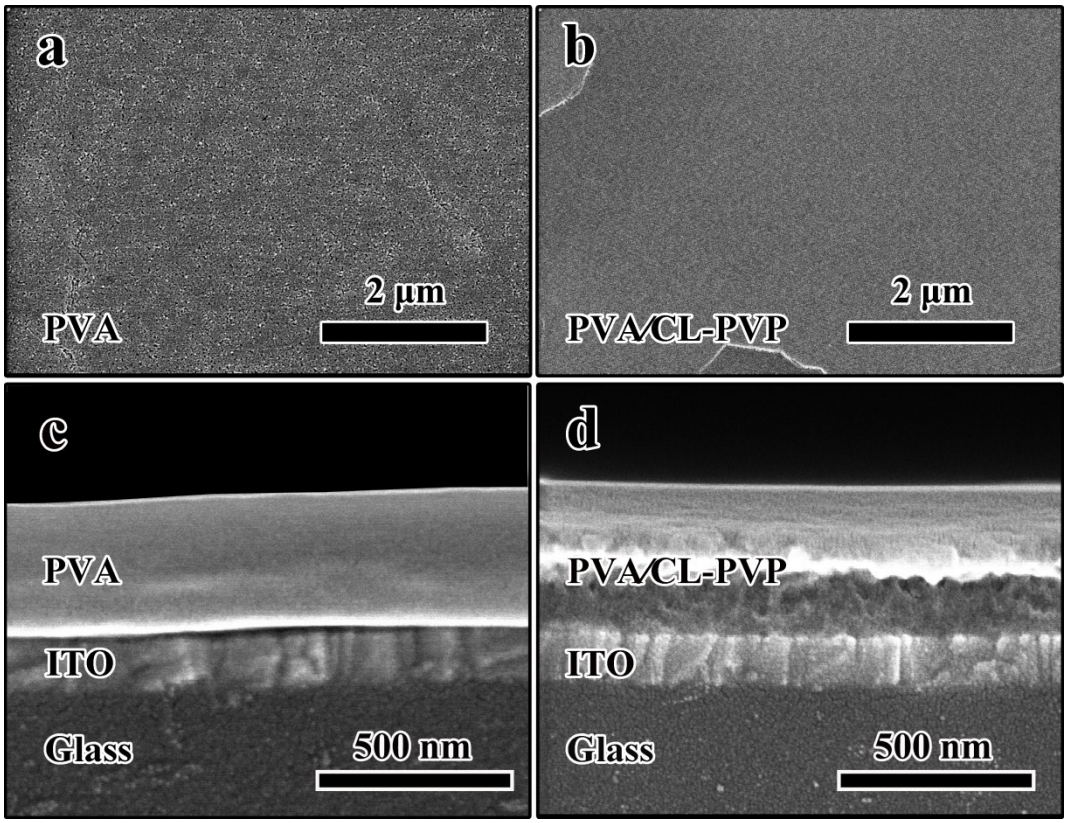

Figure S5. Top-view SEM images of the $(PEA)_2SnI_4$ thin films (a) on the PVA layer and (b) on the PVA/CL-PVP layer. Cross-sectional SEM images of the PVA film (c) and PVA/CL-PVP film (d) on ITO-glass substrates.

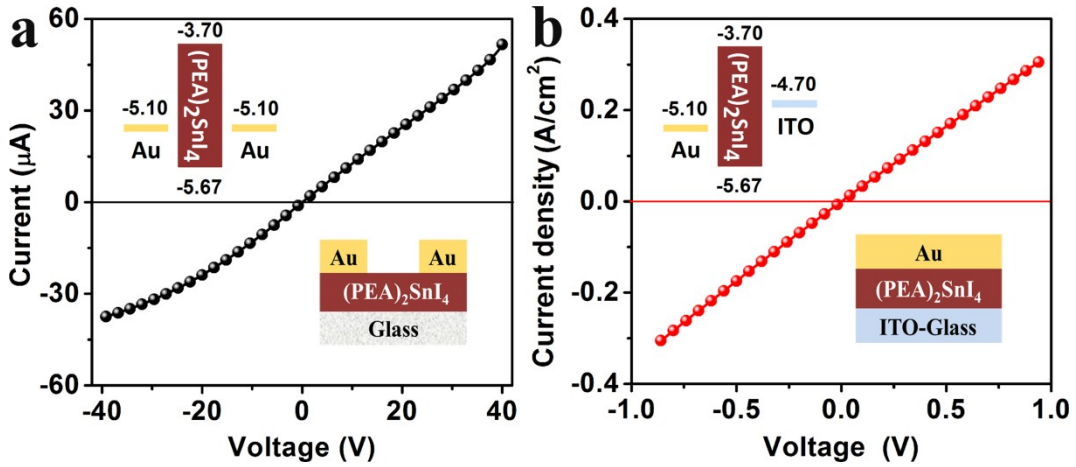

Figure S6. (a) Current-voltage and (b) current density-voltage characteristics of the lateral device and the vertical device. The insets illustrate the energy level diagrams of the two devices.

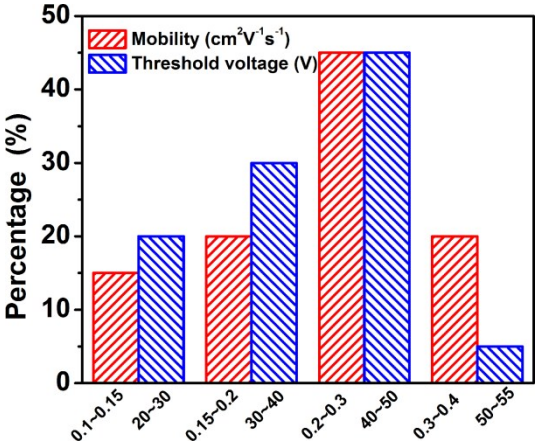

Figure S7. Histogram of the mobility and threshold voltage values of the twenty $(PEA)_2SnI_4$ FETs.

Semiconductor /dielctric	Structure	Fabrication /measurement	Channel L/W (μm)	Mobility (μ_h/μ_e) (cm^2V^{-1} s^{-1})	Threshold voltage(V)	On/off ratio	Reference
$(PEA)_2SnI_4$ /SiO_2	BGTC	Spin coating/RT in a nitrogen box	28/1000	0.62/--	--	10^4	[13]
$(PEA)_2SnI_4$ /SiO_2	BGBC	Melt-processing/LT in an inert atmosphere dry box	105/1000	2.6/--	--	10^4~10^6	[22]
$(PEA)_2SnI_4$ /SiO_2	BGTC	Vacuum deposition/RT	75/10000	0.78/--	-1.7	10^5	[23]
$(PEA)_2SnI_4$ /SiO_2	BGBC	Spin coating/RT in vacuum (10^{-5} Pa)	95/2000	3.8/--	-30	10^6	[9]
	BGTC			9.1/--	-26		
$(PEA)_2SnI_4$ /SiO_2	BGTC	Spin coating/RT in an N_2 glove box	50/1000	1.2/--	9.6~15.3	10^3	[29]
$(PEA)_2SnI_4$ /Cytop	TGTC	Spin coating/RT in vacuum (10^{-5} Pa)	95/2000	15/--	-22	10^6	[9]
$(PEA)_2SnI_4$ /Cytop	TGTC	Spin coating/RT in vacuum (10^{-5} Pa)	95/2000	--/0.6~1.5	47~53	10^4	[26]
$(PEA)_2SnI_4$ /P(VDF-TrFE)	BGBC	Spin coating/RT in nitrogen box	100/4000	0.04/--	--	~10^5	[27]
$(PEA)_2SnI_4$/ PVA/CL-PVP	BGTC	Spin coating/RT in air	50/1000	0.33/--	20	10^2~10^3	This work

Table S1. Summary of the device parameters for previously reported perovskite FETs as well as the devices in this work, indicating structure, fabrication technique, measurement, and channel length and width. BGTC, BGBC and TGTC represent bottom-gate top-contact, bottom-gate bottom-contact, and top-gate top-contact, respectively. RT and LT are the abbreviations of room temperature and low temperature, respectively.

References

1. M. E. Roberts, N. r. Queraltó, S. C. B. Mannsfeld, B. N. Reinecke, W. Knoll and Z. Bao, *Chemistry of Materials*, 2009, **21**, 2292-2299.
2. M. Yi, Y. Guo, J. Guo, T. Yang, Y. Chai, Q. Fan, L. Xie and W. Huang, *J. Mater. Chem. C*, 2014, **2**, 2998-3004.
3. C. Chen, X. Zhang, G. Wu, H. Li and H. Chen, *Advanced Optical Materials*, 2017, **5**, 1600539.