Electronic Supporting Information

$(C_6H_5NH_3)BiI_4$: A Lead-Free Perovskite with >330 Days Humidity Stability for Optoelectronic Applications

Xiao-Lei Li, Li-Li Gao, Bin Ding, Qian-Qian Chu, Zhen Li, and Guan-Jun Yang*

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

Corresponding author:

*Guanjun Yang, E-mail: ygj@mail.xjtu.edu.cn.

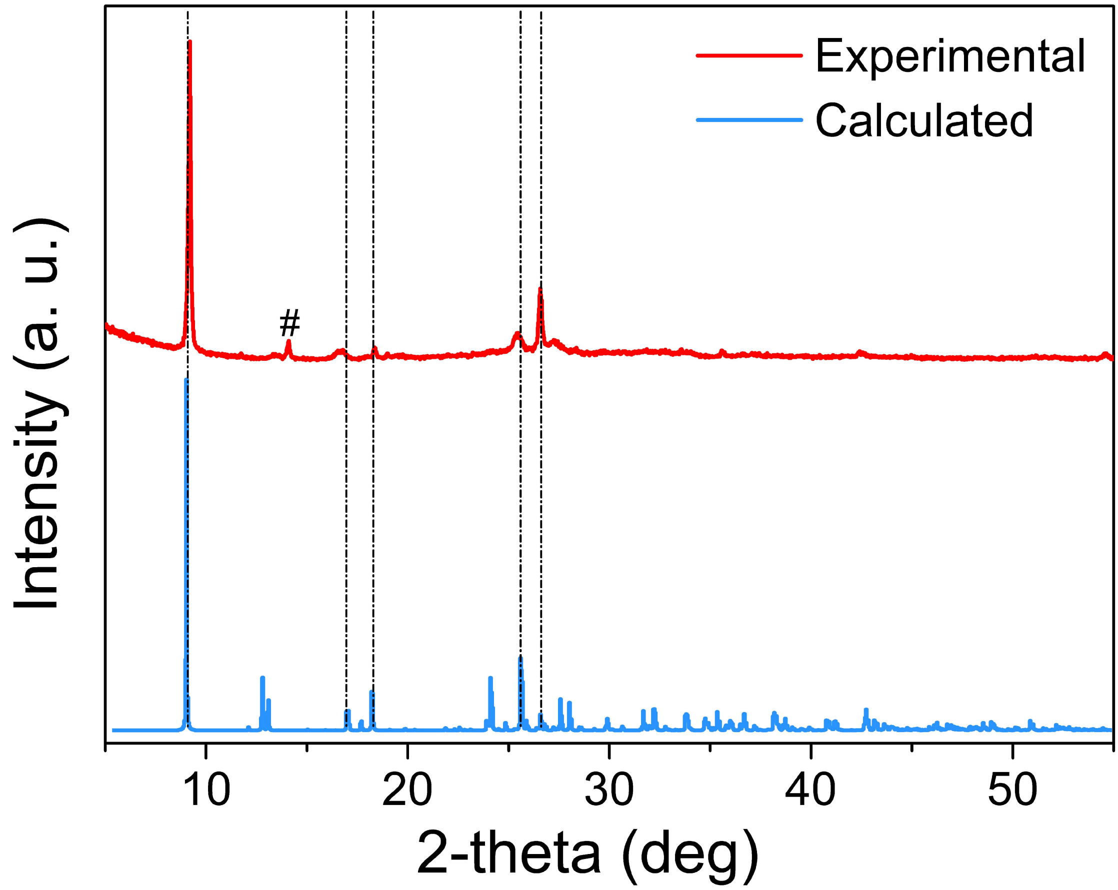

Fig. S1. Experimental and calculated XRD patterns of $(C_6H_5NH_3)BiI_4$ film. The calculated XRD pattern was performed using Reflex module package in Materials Studio.[1, 2]

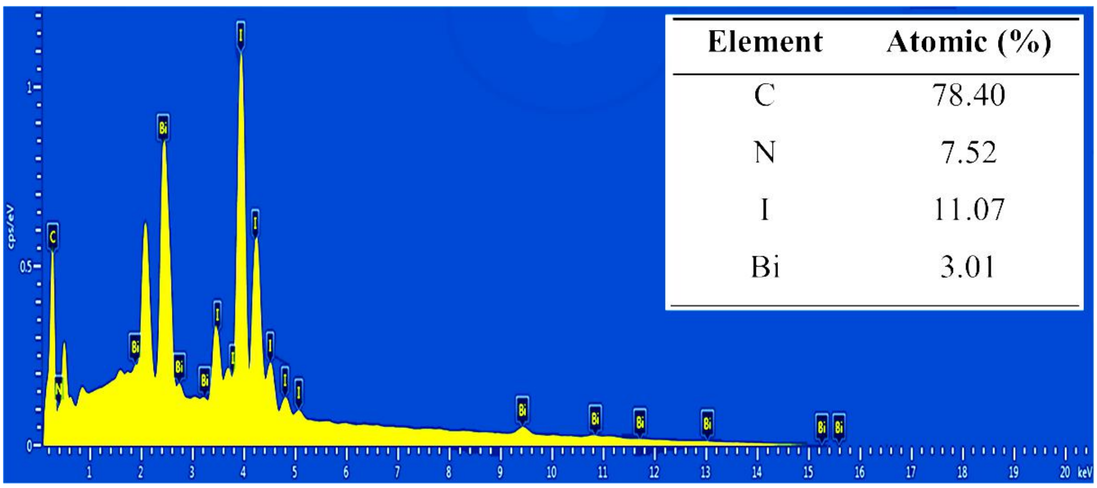

Fig. S2. EDS of $(C_6H_5NH_3)BiI_4$ film fabricated by heat treatment.

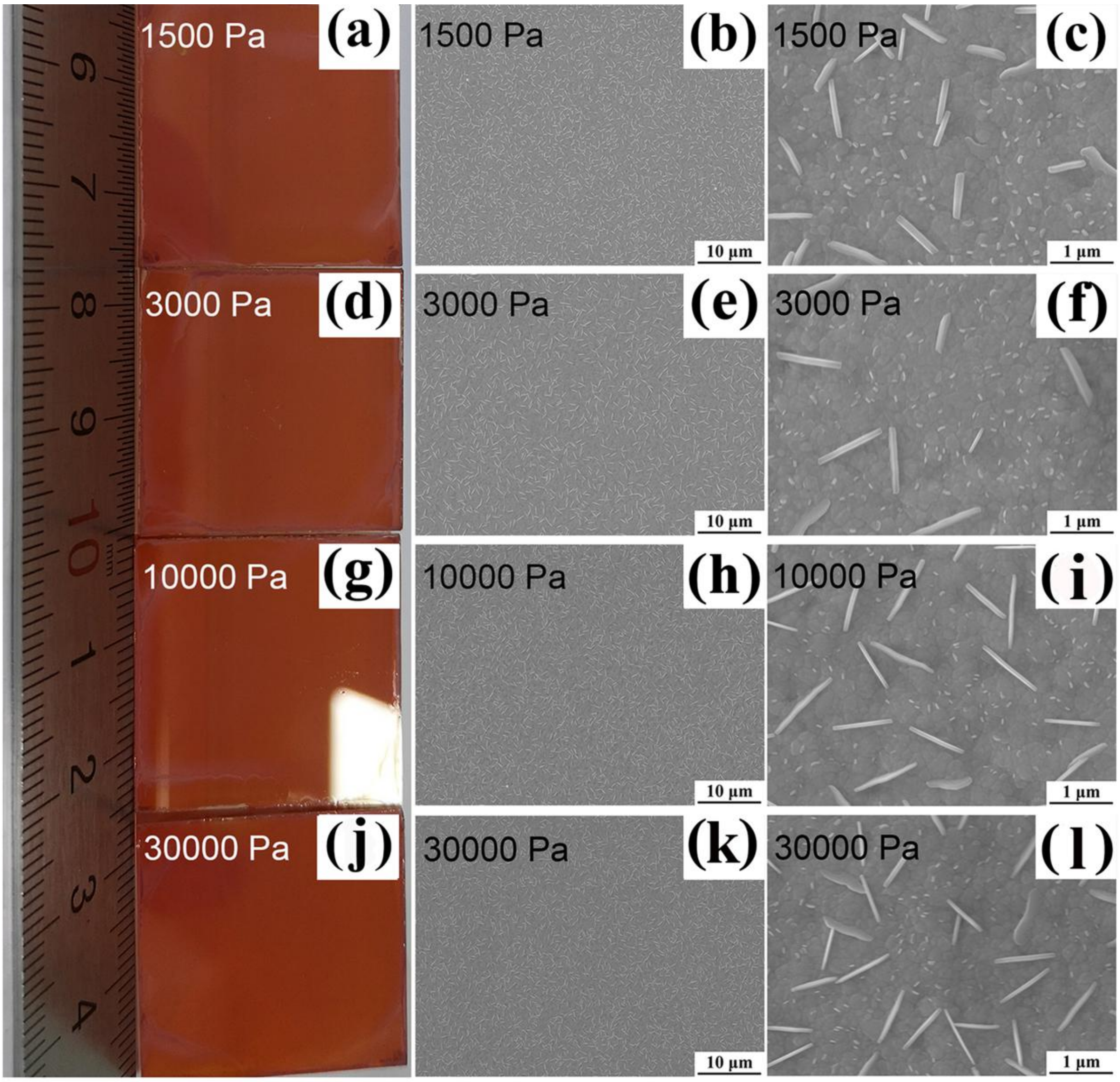

Fig. S3. Photographs and SEM images of $(C_6H_5NH_3)BiI_4$ perovskite films fabricated by gas pump treatment at different pressures: (a, b, c) 1500 Pa, (d, e, f) 3000 Pa, (g, h, i) 10000 Pa, and (j, k, l) 30000 Pa. The white area in Fig. S3g is the reflection of lamplight.

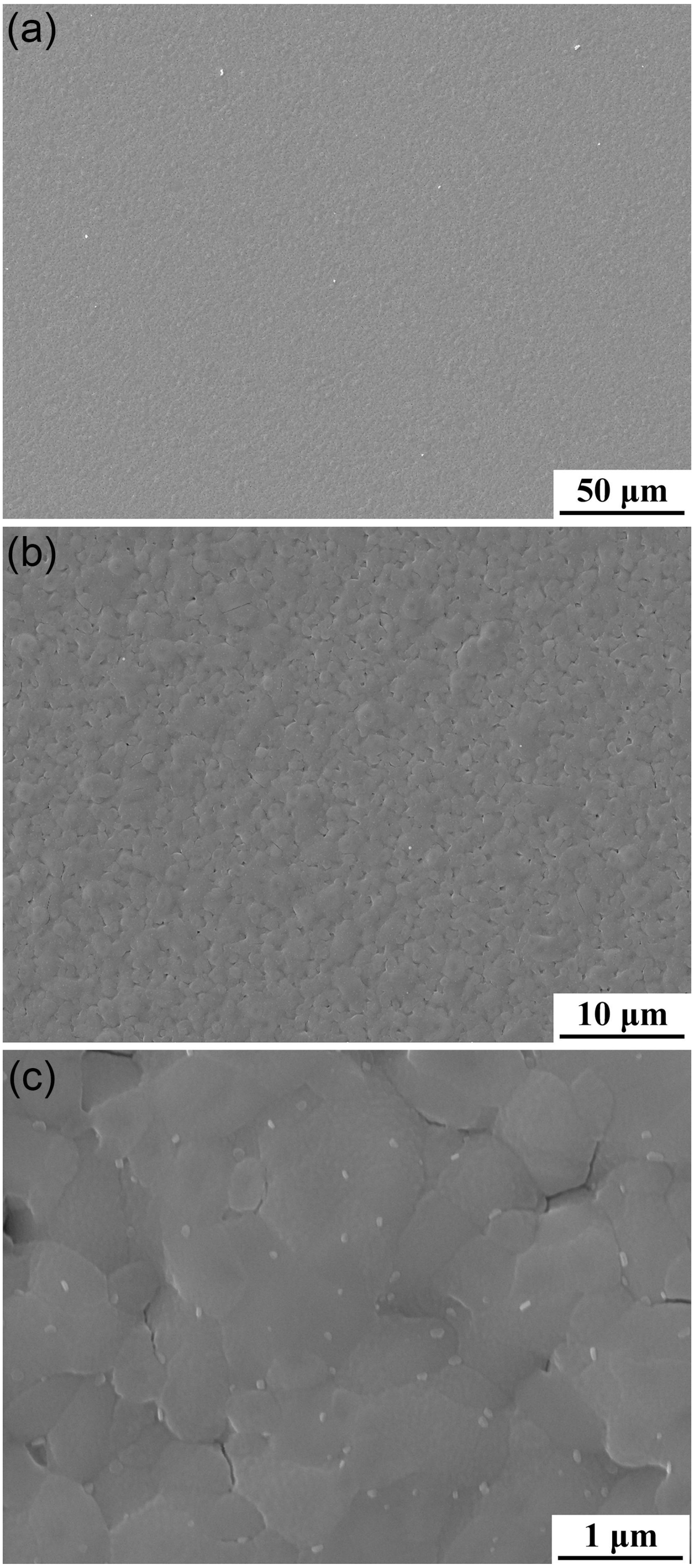

Fig. S4. SEM images of $(C_6H_5NH_3)BiI_4$ film without gas pump treatment (i. e. heat treatment, ethanol as solvent) at different magnitude: (a) 1000x , (b) 5000x, and (c) 50000x.

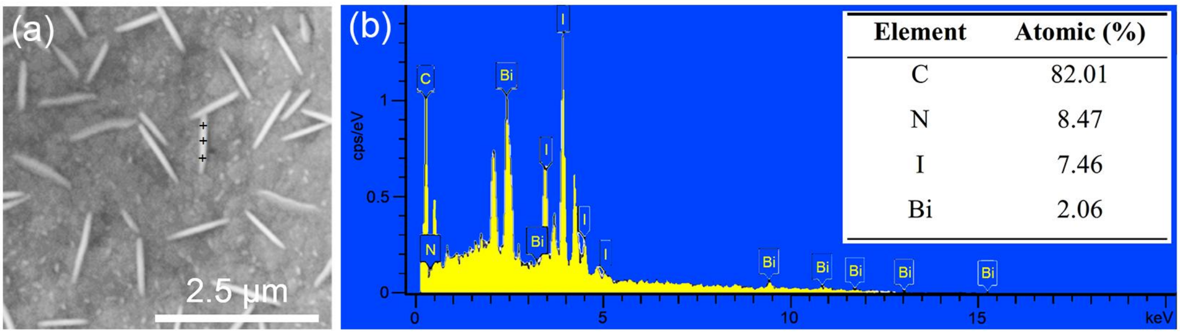

Fig. S5. SEM image (a) and EDS (b) of $(C_6H_5NH_3)BiI_4$ film with rod-like crystals.

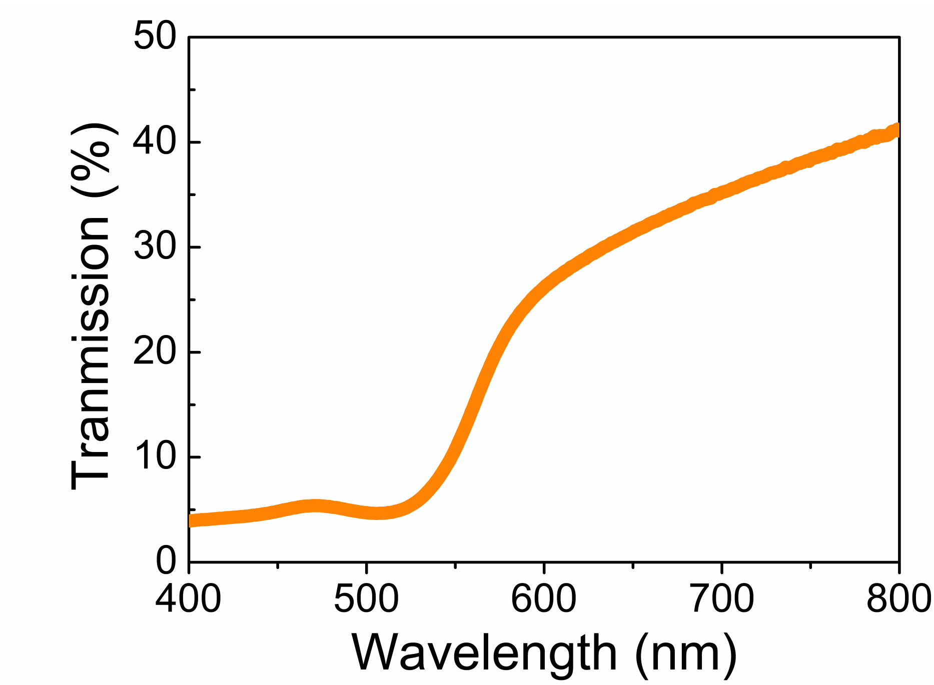

Fig. S6. Transmittance spectrum of $(C_6H_5NH_3)BiI_4$ film spin-coated on FTO glass.

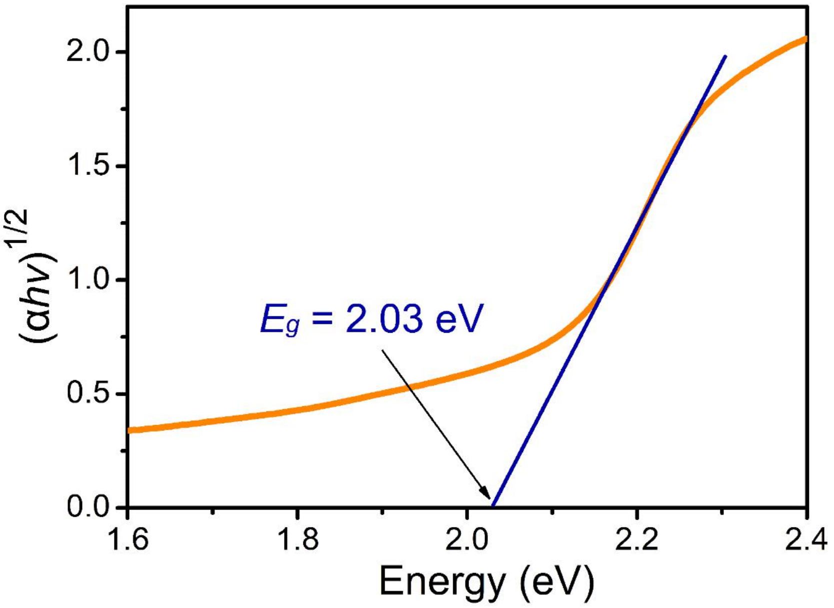

Fig. S7 *Tauc plot* of $(C_6H_5NH_3)BiI_4$ film from UV–Vis spectrum to determine E_g under the assumption of indirect band gap.

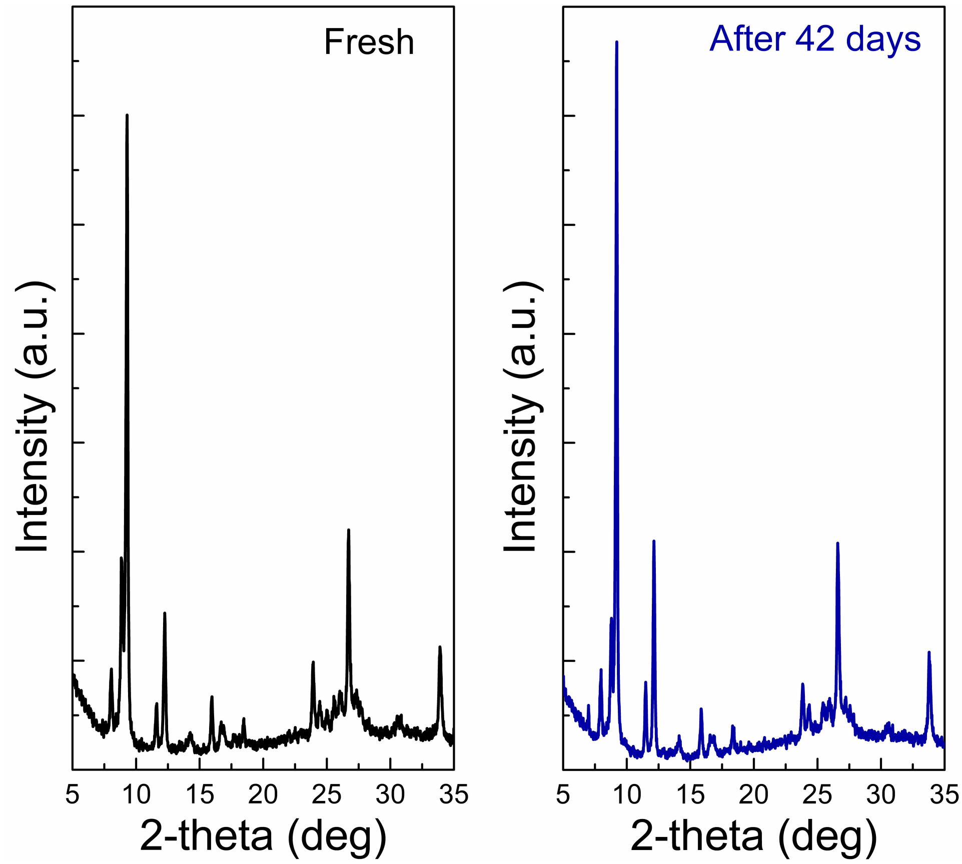

Fig. S8. Enlarged XRD patterns of $(C_6H_5NH_3)BiI_4$ film as-prepared (left) and after storage in ambient air (relative humidity of 50−70%) for 42 days (right).

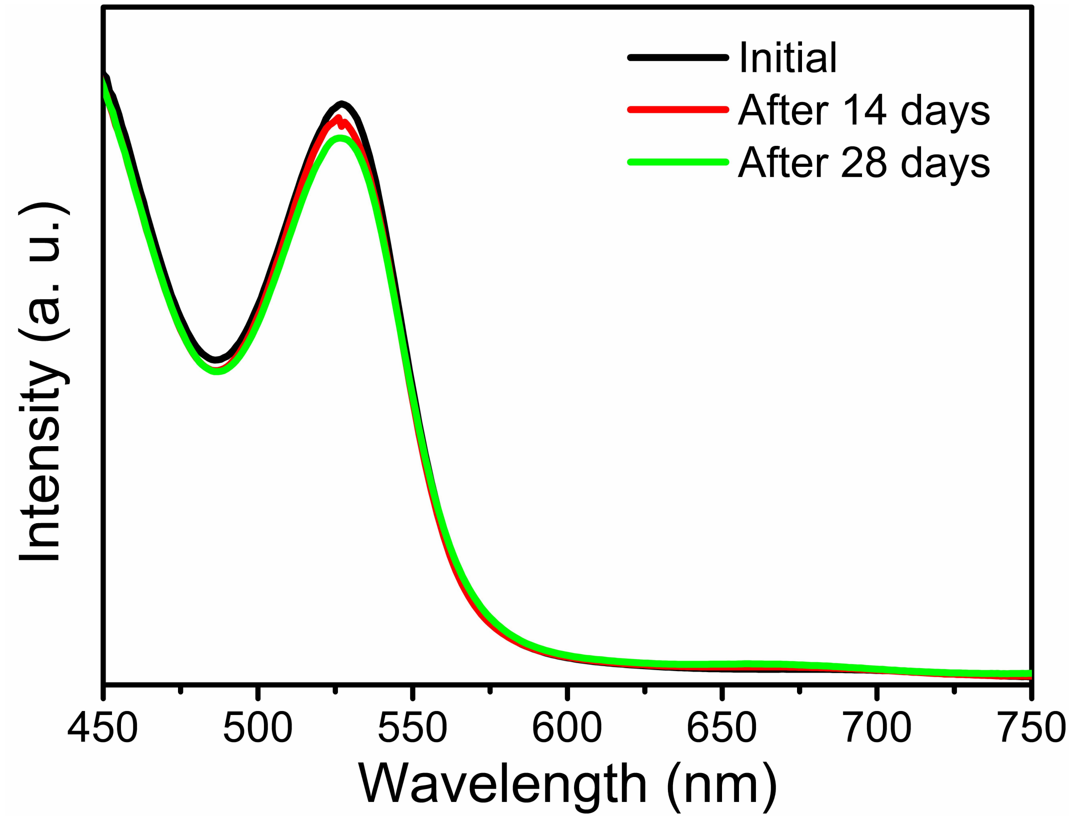

Fig. S9. UV−Vis spectra of $(C_6H_5NH_3)BiI_4$ thin film prepared by eco-friendly gas pump treatment technique before and after storage in ambient air for 14 and 28 days.

Table S1. Summary of ambient stability tests of Pb-free halide perovskite materials reported in the literature.

Types	Compound	Test period (d)	Test condition	Stability	Ref.
All-inorganic	Cs_2TiBr_6	0.25	80% RH	stable	[3]
	$AgBi_2I_7$	10	–	stable	[4]
	$Cs_3Bi_2I_9$	30	<10% RH	stable	[5]
	Cs_2NaBiI_6	150	70% RH	stable	[6]
Inorganic-organic	$C_6H_8NBiI_4$	7	–	stable	[7]
	PMA_2CuBr_4	7	60% RH	stable	[8]
	$MA_3Bi_2I_9$	25	61% RH	stable	[9]
	$MA_3Sb_2ClxI_{9-X}$	30	10% RH	stable	[10]
	$PhABiI_4$	334	50-70% RH	stable	Our work

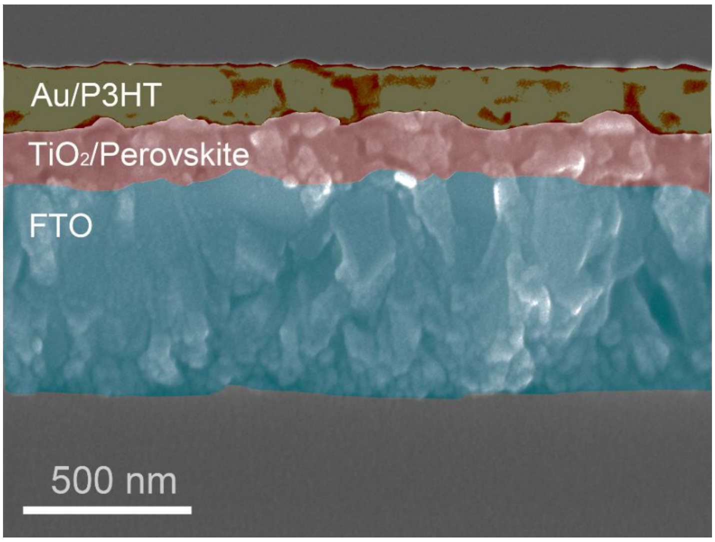

Figure S10. SEM image of a $(C_6H_5NH_3)BiI_4$-based perovskite solar cell.

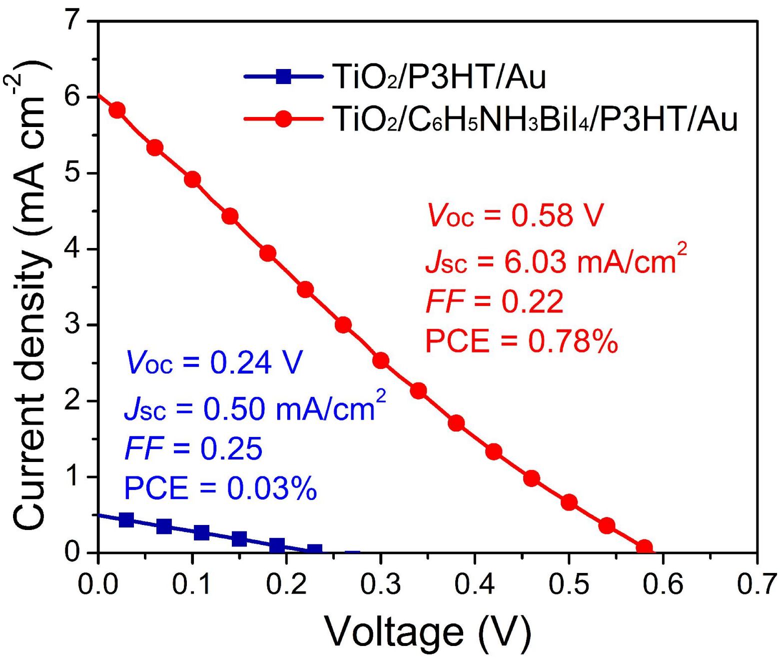

Fig. S11. Forward *J–V* curves for devices with $(C_6H_5NH_3)BiI_4$ absorber (red) and reference cell without light absorber (blue) measured under simulated AM1.5 100 mW/cm^2 illumination.

Table S2 Comparison of initial photovoltaic parameters of devices based on Pb-free and stable organic–inorganic perovskite materials.

Light absorber	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	PCE [%]	Year	Ref.
$(CH_3NH_3)_3Bi_2I_9$	0.68	0.52	33	0.1%	2015	[5]
$(CH_3NH_3)_3Sb_2I_9$	0.90	1.00	55	0.5%	2016	[11]
$(NH_4)_3Sb_2I_9$	1.03	1.15	43	0.5%	2017	[12]
$[C_5H_6N]BiI_4$	0.62	2.71	54	0.9%	2017	[7]
$[C_3H_5N_2S]BiI_4$	0.37	3.29	39	0.5%	2018	[13]
$[(CH_3NH_3)_3Bi_2Cl_9]_n$	0.43	–	–	0.0001%	2018	[14]
$(C_6H_5CH_2NH_3)_2CuBr_4$	0.68	0.73	41	0.2%	2018	[8]
$C_6H_5NH_3BiI_4$	0.58	6.03	22	0.78%	2019	This work

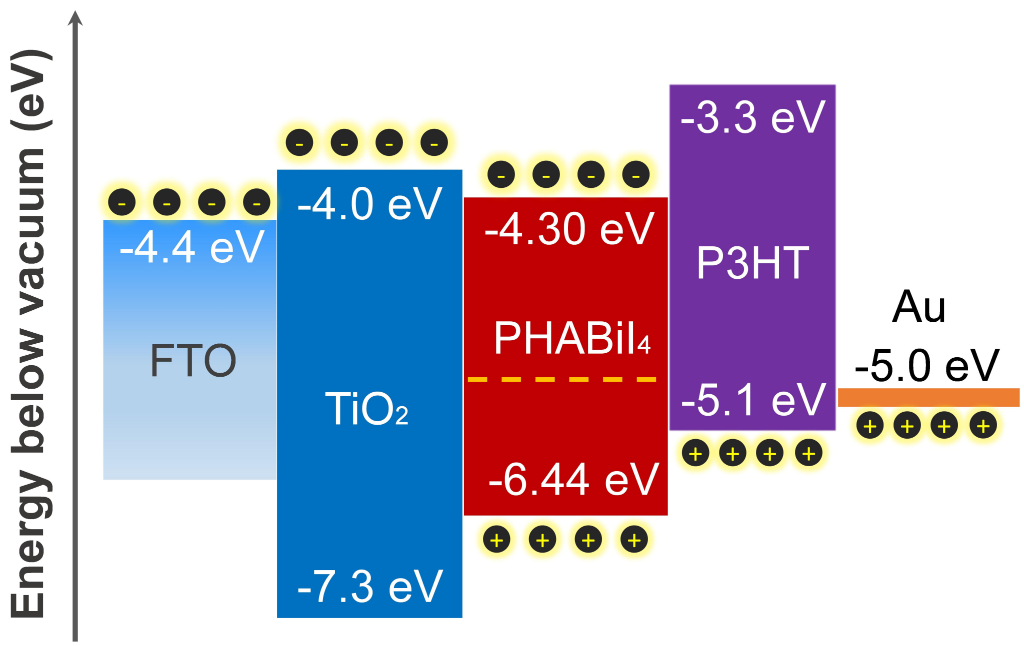

Fig. S12. Schematic energy band diagram of a $(C_6H_5NH_3)BiI_4$ solar cell. The energy levels of TiO_2 and P3HT were extracted from literature.[15]

Fig. S13. Photograph of $(C_6H_5NH_3)BiI_4$ precursor solution.

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