

1 **Multifunctional ytterbium oxide buffer for perovskite solar cells**

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33

34 **Summary**

35 **Perovskite solar cells (PSCs) comprise a solid perovskite absorber sandwiched**
36 **between multiple layers of different charge-selective materials, ensuring uni-**
37 **directional current flow and high voltage output of the devices^{1,2}. A “buffer material”**
38 **between the electron-selective layer (ESL) and the metal electrode in p-**
39 **type/intrinsic/n-type (p-i-n) PSCs (also known as inverted PSCs) allows electrons to**
40 **flow from the ESL to the electrode³⁻⁵. Also, it acts as a barrier inhibiting the inter-**
41 **diffusion of harmful species in or degradation products out of the perovskite**
42 **absorber⁶⁻⁸. Thus far, evaporable organic molecules^{9,10} and atomic-layer-deposited**
43 **metal oxides^{11,12} have proven successful, but each has specific imperfections. Here, we**
44 **report a chemically stable and multifunctional buffer material, ytterbium oxide**
45 **(YbO_x), for p-i-n PSCs *via* scalable thermal evaporation deposition. We employed this**
46 **YbO_x buffer into the p-i-n PSCs with a narrow-bandgap (NBG) perovskite absorber,**
47 **yielding a certified power conversion efficiency (PCE) of over 25%. We also**
48 **demonstrate the broad applicability of YbO_x in enabling highly efficient PSCs from**
49 **various types of perovskite absorber layers, delivering state-of-the-art efficiencies of**
50 **20.1% for the wide-bandgap (WBG) perovskite absorber and 22.1% for the mid-**
51 **bandgap (MBG) perovskite absorber, respectively. Moreover, when subjected to**

52 **ISOS-L-3 accelerated ageing, encapsulated devices with YbO_x exhibit markedly**

53 **enhanced device stability.**

54

55 The PCE of single-junction p-i-n PSCs (also referred to as inverted PSCs) has surpassed
56 25% through passivation methodologies^{3-5,13-15}. However, the published operational
57 stability of p-i-n PSCs under stringent test conditions still lags behind commercially viable
58 solar panels¹⁶⁻¹⁸. Though multiple factors are responsible for device degradation under
59 operating conditions¹⁹⁻²¹, ion migration under realistic operational conditions represents a
60 significant challenge as it is almost ubiquitous within a device. Electrical bias and
61 illumination-induced ion migration within a perovskite absorber layer can inevitably vary
62 the chemical composition at the nano- and micro-scale^{19,21,22}, inducing higher chemical
63 heterogeneity, increased non-radiative recombination centers and subsequent initial sites
64 where device degradation occurs^{2,23}. Furthermore, these mobile ions from the perovskite
65 absorber can diffuse into the charge-selective layers and may accumulate at the metal
66 electrode interface. The accumulated ions have been proven to corrode the metal
67 electrodes^{7,24}, damaging the integrity of the metal electrode and degrading device stability.
68 Another key concern for long-term instability is the metal diffusion into the electron-
69 selective and perovskite layers, which may lead to the formation of metal halides and
70 weakened device stability^{7,25,26}.

71 Attempting to introduce an effective buffer layer between the ESL and the metal electrode
72 to block atom and ion movement between the perovskite and metal layers (in both
73 directions, **Extended Data Fig. 1a**) is of technological interest in improving overall device

74 performance⁶⁻⁸. In this case, the buffer layer must facilitate the directional flow of electrons
75 from the buffer to the metal electrode, ensuring efficient electron collection of the PSCs.
76 The method for depositing the buffer layer must be compatible with underlying materials
77 such as (6,6)-Phenyl C₆₁ butyric acid methyl ester (PCBM) and C₆₀. Moreover, an ideal
78 buffer layer can effectively prevent the permeation of external harmful species like oxygen
79 and moisture from the air. To date, bathocuproine (BCP), the most commonly used buffer
80 material, can be processed with scalable thermal evaporation in p-i-n PSCs^{5,9}.
81 Unfortunately, BCP suffers from poor thermal stability under the protocol temperature of
82 85°C by the International Summit on Organic Photovoltaic Stability (ISOS) protocols,
83 which will likely limit long-term operational stability^{12,22,27-29}. Low work-function oxides,
84 including zinc oxide (ZnO) nanoparticles, compact tin oxide (SnO₂) layer, and aluminum-
85 doped zinc oxide (AZO) nanoparticles, have also been applied as buffer materials in p-i-n
86 PSCs to replace the BCP or to form bilayer buffers^{11,12}. Yet, these oxides either are
87 challenging for large-scale fabrication or require dedicated instruments and expensive
88 fabrication precursors, which contradicts cost-effective practical applications. An
89 intrinsically stable and multifunctional material, YbO_x, which can be deposited by the
90 scalable thermal evaporation approach, is a compelling buffer material for efficient and
91 stable p-i-n PSCs.

92 **Properties of ytterbium oxide**

93 Yb with a low Gibbs free energy has a strong tendency to form YbO_x when exposed to
94 oxygen (**Supplementary Note 1, Extended Data Fig. 1b**). The YbO_x that can be processed
95 with thermal evaporation (**Extended Data Fig. 1c**) shows great promise of commercial
96 applications (**Supplementary Note 2, Supplementary Tables 1 and 2**). To understand the
97 oxidation of Yb, we first thermally evaporated a few nanometers of Yb films on a large-
98 scale indium tin oxide (ITO) substrate (100 cm^2) in the device fabrication vacuum chamber
99 with a base pressure of 10^{-4} Pa. The sampling data from different areas of the sample shows
100 identical YbO_x states (**Extended Data Fig. 2**). This rapid oxidation associated with metal
101 Yb is further demonstrated by the color change of the polished Yb metal surfaces before
102 and after oxidation (**Extended Data Fig. 3**). We then studied the detailed oxidation
103 dynamics of the clean Yb^0 surface by tracking the oxidation process over time using in-situ
104 photoelectron X-ray spectroscopy (XPS) (**Extended Data Fig. 4, Supplementary Table**
105 **3**). These results indicate that the Yb film (with a thickness of a few nanometers) deposited
106 on the large-area ITO substrate can be fully oxidized in a few minutes when upscaling in a
107 device fabrication vacuum chamber with a base pressure of 10^{-4} Pa (see details in
108 **Supplementary Note 3**). Such benefits eliminate the additionally dedicated oxidation step,
109 which is usually required for other oxides processed with thermal evaporation³⁰.

110 **Fig. 1a-c** shows the high-resolution TEM (HRTEM) images and the corresponding fast
111 Fourier transform (FFT) patterns of the Yb film. The HRTEM images and FFT patterns

112 feature the crystalline structure corresponding to a face-centered cubic system with space
113 group 225 (Fm3m) visualized from [0-11] direction in the selected red rectangle region.
114 By clarifying the Yb natural oxidation through XPS spectra (**Fig. 1d, e**)^{31,32}, the resulting
115 YbO_x exhibits a broad and continuous halo in the typical FFT pattern, indicative of the
116 amorphous atomic arrangement (**Extended Data Fig. 5**)³³. The amorphous characteristics
117 of the YbO_x films are also confirmed through grazing-incidence wide-angle X-ray
118 scattering (GIWAXS) (**Extended Data Fig. 6**). The energy-dispersive X-ray (EDX)
119 chemical composition map for the YbO_x film suggests a spatially homogeneous distribution
120 of both Yb and O elements in the films is spatially homogeneous (**Supplementary Fig. 1**).
121 The reflection electron energy loss spectroscopy (REELS) spectrum shows the surface
122 bandgap of the YbO_x is as high as 5.5 eV (**Fig. 1f**)³⁴, which is transparent to visible light
123 wavelengths. Critical information associated with the electronic structure, including work
124 function, valence band maximum (VBM), and conduction band minimum (CBM), are
125 quantified by combining ultraviolet photoemission spectroscopy (UPS) analyses (**Fig. 1g**)
126 with the REELS data. These results above suggest that the YbO_x film is n-type, with a
127 Fermi level of 3.08 eV from the vacuum and a CBM of 1.26 eV from the vacuum (**Fig. 1h**).

128 **Multifunctional role of interfacial YbO_x**

129 **Fig. 2** shows XPS data on the variation of chemical constituents in the electron-selective
130 layer and its interface with the metal electrode measured from samples with (target) and

131 without (control) the YbO_x buffer layer before and after accelerated ageing in ambient air
132 (relative humidity, 80%) at 80°C for 5 h. The samples consist of
133 substrate/perovskite/ C_{60} /Cu (control) and substrate/perovskite/ C_{60} / YbO_x /Cu (target). A
134 mechanical lift-off approach was used to delaminate the Cu electrode from the rest of the
135 sample stacks³⁵. The delaminated Cu is referred to as the Cu side, and the other is the
136 substrate side (**Supplementary Fig. 2**). **Supplementary Fig. 3** shows scanning electron
137 microscope (SEM) images of the delaminated surfaces of both control and target samples.
138 The buried organic C_{60} layer for the substrate side was removed using gas cluster ion beam
139 (GCIB) sputtering in order to probe throughout the layer stack.

140 **Fig. 2a, b** shows the Cu 2p XPS depth profiling of the substrate side before and after ageing.
141 Note that the Cs Auger signal (highlighted in orange color) is used to probe the perovskite
142 layer in this observation. The data show a noticeable decrease in the Cu 2p XPS peak
143 intensity of the fresh control sample (without YbO_x) after the 60 s of GCIB sputtering, and
144 the Cu 2p XPS peak intensity is below the instrument limitation with increasing the
145 sputtering time. In contrast, the Cu 2p XPS peaks for the aged control samples remain
146 detectable after extended GCIB sputtering to such as 360 s (**Fig. 2b**). While at 720 s, Cu
147 2p XPS peaks and significant Cs Auger signals are simultaneously detected for the aged
148 control sample. This experimental observation indicates that Cu diffusion exists in the aged
149 control samples. When the YbO_x buffer layer is inserted between the C_{60} and Cu, the

150 distribution of the Cu species into the C₆₀ and perovskite underneath is not detected for
151 both fresh and aged target samples, as shown in **Fig. 2c**. Next, we probed the chemical
152 changes on the delaminated Cu surfaces of both control and target samples by tracking the
153 Cu LMM Auger peaks of the delaminated Cu side after ageing. A peak exists at around
154 571 eV for the aged control sample without YbO_x (**Fig. 2d**). This result indicates that Cu
155 oxidation happens in the aged control samples, consistent with the color change of the Cu
156 electrode (control) after accelerated ageing in ambient air (relative humidity, 80%) at 80°C
157 for 5 h (**Supplementary Fig. 4**). However, the Cu oxidation peak is not observed in the
158 aged target samples (with YbO_x) (**Fig. 2e**)^{23,36}. The depth-profiling data show that the
159 chemical state of the YbO_x remains the same throughout the thickness before and after
160 accelerated ageing (**Fig. 2f**).

161 The UPS depth profiling analysis based on the real device stacks reveals that the insertion
162 of YbO_x can reduce the work function of the contact interface compared to the control
163 sample without YbO_x (**Supplementary Fig. 5**). One such variation brings a positive impact
164 on electron collection at the Cu electrode interface. To reveal the charge-carrier transport
165 properties of the YbO_x buffer, two devices with 20 alternative layers of YbO_x (2 nm) and
166 YbO_x (5 nm)/Cu (1 nm) [for example, ITO/[YbO_x (2 nm)]₂₀/Cu (100 nm) and ITO/[YbO_x
167 (5 nm)/Cu (1 nm)]₂₀/Cu (100 nm)] were prepared. We confirm that the YbO_x used in the
168 charge-carrier transport measurements shows no metallic states and instead exhibits a

169 considerable density of in-gap states near the Fermi level (**Extended Data Fig. 7a, b**). By
170 measuring the temperature dependence of current density–voltage (J – V) characteristics of
171 the devices with ITO/[YbO_x (2 nm)]₂₀/Cu (100 nm) and ITO/[YbO_x (5 nm)/Cu (1 nm)]₂₀/Cu
172 (100 nm) (**Extended Data Fig. 7c, d** and **Extended Data Fig. 8**), we find that the charge-
173 carrier transport inside the YbO_x follows a phonon-assisted electron hopping from one
174 localized state to another rather than through the drift of Bloch wave described in the typical
175 energy-band theory (**Supplementary Note 4**). This physical process was originally
176 proposed by Mott³⁷, who gave the temperature-conductivity dependence law below:

$$177 \quad \sigma = \sigma_0 \exp\left(-B/T^{\frac{1}{4}}\right) \quad (1)$$

178 where σ_0 is a pre-factor, and B depends on the radial extension of the wave functions and
179 density of states. Herein, we illustrate phonon-assisted electron hopping *via* unoccupied
180 localized states of the YbO_x buffer layer when electrons flow from C₆₀ to Cu (**Fig. 3a**).

181 **Photovoltaic performance enhancement**

182 To assess the impact of the YbO_x buffer layer on device performance, we fabricated full
183 devices using perovskites with three different typical bandgaps. The cross-sectional and
184 top-view SEM images for these perovskites are shown in **Supplementary Fig. 6**.
185 **Supplementary Fig. 7** displays the optoelectronic properties of the associated perovskites
186 with various bandgaps. Firstly, we evaluated the photovoltaic performances of the p-i-n
187 PSCs based on an NBG perovskite absorber [Rb_{0.05}Cs_{0.05}MA_{0.05}FA_{0.85}Pb(I_{0.95}Br_{0.05})₃]. The

188 perovskite absorber was post-treated with 3-(Aminomethyl)pyridine to suppress non-
189 radiative recombination at the interface³. **Fig. 3b** displays device configurations of the p-i-
190 n PSCs with YbO_x and illustrates the amorphous nature of the YbO_x buffer. The optimal
191 thickness for the YbO_x layer in this work is around 1.5 nm (**Supplementary Fig. 8**).

192 From *J–V* scanned results, the champion PSC with YbO_x exhibits a remarkable PCE of
193 25.2% [an open-circuit voltage (*V*_{OC}) of 1.16 V, a fill factor (FF) of 0.83, and a short-circuit
194 current density (*J*_{SC}) of 26.1 mA cm⁻²] (**Fig. 3c** and **Extended Data Table 1**). The steady-
195 state power output (SPO) of our YbO_x-based p-i-n PSCs is ~24.7% under standard
196 simulated 1-sun illumination, AM 1.5G irradiance (**Fig. 3c**), and the YbO_x-based devices
197 show negligible hysteresis in nature (**Supplementary Fig. 9**). Note that a MgF₂
198 antireflection coating was used to minimize the light reflection therefore to maximize the
199 photocurrent of the p-i-n PSCs (**Supplementary Table 4**). To further validate our finding,
200 we sent one of our non-encapsulated YbO_x-based NBG PSCs to an accredited institution
201 of the Photovoltaic and Wind Power Systems Quality Test Center (Chinese Academy of
202 Science, China) for external certification. We obtained a certified PCE of 25.09%
203 (**Supplementary Fig. 10**), which is among the highest PCEs of p-i-n PSCs and represents
204 the best PCE of p-i-n PSCs with an inorganic buffer layer (**Supplementary Tables 5 and**
205 **6**). Our experiments further validate the universality of the YbO_x buffer layer in the p-i-n
206 PSCs with MBG and WBG perovskite absorbers. The MBG PSCs with YbO_x deliver

207 decent performance with a champion PCE of 22.1% (**Fig. 3d**). In particular, the YbO_x-
208 based WBG devices yield an impressive PCE of up to 20.1% [a V_{OC} of 1.30 V, an FF of
209 0.82 and a J_{SC} of 18.6 mA cm⁻²] (**Fig. 3e**). To our knowledge, this respectful PCE is among
210 the highest PCEs for p-i-n PSCs with WBGs of 1.75–1.80 eV (**Supplementary Table 7**).
211 Moreover, we find that p-i-n PSCs with YbO_x show high reproducibility and minor batch-
212 to-batch variations in device performance regardless of the perovskite bandgap (**Fig. 3f**,
213 **Supplementary Figs. 11, 12**).

214 It is clear that all these p-i-n PSCs have achieved prominent V_{OC} in **Fig. 3g**, which are close
215 to or even surpass 90% of the radiative limit versus the bandgap energy³⁸. Furthermore,
216 external quantum efficiencies of the electroluminescence (EQE_{EELS}) for the YbO_x-based p-
217 i-n PSCs with NBG and WBG perovskite absorbers (**Supplementary Fig. 13**) present 5.12%
218 (NBG) and 0.97% (WBG), respectively. Under such conditions, derived from the EQE_{EEL},
219 we calculated the QFLS values of the PSCs containing the different absorbers to be 1.159
220 eV (NBG) and 1.289 eV (WBG), respectively, consistent with the obtained V_{OC} from the
221 J - V scans (**Supplementary Note 5**). Moreover, the integrated J_{SC} values of the champion
222 NBG-, MBG-, and WBG-based PSCs, where their bandgaps are calculated to be 1.54 eV,
223 1.59 eV, and 1.77 eV (**Supplementary Fig. 14**), are 25.7 mA cm⁻², 22.1 mA cm⁻², and
224 18.3 mA cm⁻², respectively (**Fig. 3h**).

225 **Thermal and operational stability**

226 We tested the thermal stability of the PSCs with BCP or YbO_x (encapsulated using glass
227 covers sealed by epoxy resin). The encapsulated PSCs are stored at 85°C in the dark in a
228 nitrogen-filled glovebox. **Fig. 4a** compares results of the thermal stability for the NBG-
229 based PSCs with BCP or YbO_x buffer layers. Compared to the PSCs with BCP, the YbO_x-
230 based device exhibits a slight increase in the PCEs initially (<100 h) and retains 98% of its
231 initial PCE after 500 h. By contrast, the BCP-based device shows a sharp PCE drop upon
232 exerting thermal stress, and only 82% of its initial PCE can be retained after 500 h.
233 Similarly, in the WBG-based PSCs, the YbO_x-based device exhibits enhanced thermal
234 stability (**Fig. 4b**). However, the WBG-PSCs with either BCP or YbO_x buffer layers
235 degrade at faster rates compared to NBG-based PSCs. Such a difference correlates with the
236 inherently poor stability of the WBG perovskite with a high bromide ratio^{39,40}. Nonetheless,
237 the WBG-based PSCs with YbO_x can still retain 80% of its initial PCE after 500 h, whereas
238 the BCP-based device drops quickly to 75% of its initial PCE in the initial 24 h and
239 approximately 57% of device performance after 500 h.

240 We also examined the long-term operational stability tracking at the maximum power
241 output under 1-sun illumination with and without thermal stress. The tested PSCs were also
242 encapsulated and continuously illuminated by a white light-emitting diode (LED) array
243 with an intensity equivalent to 100 mW cm⁻² of AM 1.5G irradiance without active cooling.
244 The most stable NBG-based device with YbO_x maintained its initial performance for 800

245 h, and retained 97% of the initial PCE (23.5%) after 1000 h (**Fig. 4c**). In comparison, the
246 NBG-based device with BCP dropped quickly to 96% of the initial PCE after 213 h
247 (**Supplementary Fig. 15**). Notably, when subjected to multiple external stress (complied
248 with ISOS-L-3 protocols), compared to the BCP-based device, the encapsulated YbO_x -
249 based device still exhibits improved long-term operational stability tracking at maximum
250 power output point at 85°C in ambient air (relative humidity, 50%) (**Fig. 4d** and
251 **Supplementary Figs. 16, 17**). Specifically, the encapsulated devices with YbO_x retain ~85%
252 of its initial PCE (23.6%) after 500 h, which is comparable to p-i-n PSCs with SnO_2
253 (**Supplementary Table 8**). By contrast, the BCP-based device only retains 60% of the
254 initial PCE after 213 h under ISOS-L-3 test qualifications. These results indicate that the
255 PSCs with the YbO_x buffer show more substantial resistance to external stress than the
256 regular BCP-containing ones, consistent with our observation above. Note that although
257 enhanced device stability of p-i-n PSCs employing BCP buffer layers in conjunction with
258 Cr/Au electrodes has been reported in the past⁴¹, such a multilayer buffer makes the device
259 much more complex, and Au is not a scalable metal owing to its high cost (**Supplementary**
260 **Table 2**).

261 To gain more insights into the device stability improvements, we then conducted time-of-
262 flight secondary ions mass spectrometry (TOF-SIMS) measurements on full PSC devices
263 with BCP or YbO_x before and after ageing. Combining the TOF-SIMS with the depth-

264 profile XPS results (**Fig. 2, Extended Data Fig. 9, and Supplementary Fig. 18**), we
265 demonstrate that replacing BCP with YbO_x can suppress undesirable bi-directional harmful
266 species movements (such as I⁻, Cs⁺, Rb⁺, and Cu), and we find that the YbO_x is chemically
267 unreactive with the perovskites (**Fig. 4e-g**, see details in **Supplementary Note 6**). Hence,
268 we conclude that multifunctional YbO_x is advantageous for use as the buffer material from
269 various evaluation angles (**Supplementary Fig. 19**).

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360 **Figure legends**

361 **Fig. 1 | Characterization of YbO_x films.** **a**, A general high-resolution transmission
362 electron microscopy (HRTEM) image of the pure ytterbium film. The magnified HRTEM
363 image (**b**) and the corresponding fast Fourier transform (FFT) patterns (**c**) of the red
364 squared area selected in (**a**). X-ray photoemission spectroscopy (XPS) spectra of the Yb 4d
365 corresponding to the Yb³⁺ state (**d**) and O 1s (**e**). **f**, The reflection electron energy loss
366 spectroscopy (REELS) spectrum of the YbO_x film. The inset shows how the band gap is
367 determined. **g**, Ultraviolet photoelectron spectroscopy (UPS) spectra of the YbO_x film. Left,
368 secondary electron cut-off (SECO) spectrum. Right, valence band (VB) spectrum. **h**,
369 Energy levels of the YbO_x film. Key parameters shown are E_{CBM} (conduction band
370 minimum), E_{VBM} (valence band maximum), E_F (Fermi level), and E_{VAC} (vacuum level).

371 **Fig. 2. | Photoemission spectroscopy of the lift-off full devices.** Cu 2p XPS depth
372 profiling using gas cluster ion beam (GCIB) sputtering (The sputtering rate for organic
373 films is about 0.05 nm s⁻¹ using *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-
374 diamine (NPB) as the reference) detected at the substrate side of (**a**) the fresh control
375 (without YbO_x) sample and (**b**) the aged control sample (after thermal annealing at 80° C
376 in ambient air for 5 h). Control: substrate/perovskite/C₆₀/Cu. **c**, Cu 2p XPS depth profiling
377 detected at the substrate side of the fresh (up) and the aged (bottom) target samples (with
378 YbO_x, after thermal annealing at 80°C in ambient air for 5 h). Target:

379 substrate/perovskite/C₆₀/YbO_x/Cu. Cu LMM Auger spectra were detected at the Cu side of
380 (d) the aged control sample and (e) the aged target sample (after thermal annealing at 80°C
381 in ambient air for 5 h). The red line at the top shows the spectra difference, and this line is
382 obtained by using the as-delaminated spectrum (0 s, blue lines at the middle) minus Cu⁰
383 reference spectrum (black lines at the bottom)], which can be used to analyze chemical
384 states. f, Yb 4d XPS depth profiling measured at the Cu side of the fresh target sample with
385 YbO_x, before and after the accelerated ageing.

386 **Fig. 3. | Photovoltaic performance.** a, Schematic illustration of the charge-carrier
387 transport across the ESL/YbO_x/Cu interface. The carrier transport in the YbO_x buffer layer
388 is by phonon-assisted electron hopping from one localized state to another. b, Schematic
389 illustration of the device configuration of a typical p-i-n PSCs with the YbO_x buffer layer.
390 The magnified area illustrates the amorphous nature of the YbO_x buffer layer used in our
391 p-i-n PSCs. c-e, The current density–voltage (*J*–*V*) characteristics of the p-i-n PSCs with
392 various bandgaps and these devices' steady-state power output (SPO) at the maximum
393 power point under simulated AM 1.5 G illumination (inset). NBG, narrow bandgap. MBG,
394 mid-bandgap. WBG, wide bandgap. f, Power-conversion-efficiencies (PCEs) distributions
395 for p-i-n PSCs with NBG, MBG, and WBG bandgaps. The number of devices is 15 for
396 each. g, Comparison of the *V*_{OC} of state-of-the-art p-i-n PSCs with varied bandgaps. Note
397 that the data from the literature is based on the p-i-n PSCs with the BCP buffer layer. The

398 dashed line represents 90% of the radiative limit concerning the bandgap energy. **h**, The
399 external quantum efficiency (EQE) spectra of the champion p-i-n PSCs with NBG, MBG,
400 and WBG perovskites.

401 **Fig. 4. | Stability of YbO_x-based p-i-n PSCs.** Variations of the PCEs of the encapsulated
402 (a) NBG- and (b) WBG-containing PSCs with the BCP or YbO_x buffer layer aged in a
403 nitrogen-filled glove box under 85°C in the dark. **c**, The maximum power point tracking
404 (MPPT) curve of an encapsulated NBG-containing PSC with YbO_x under continuous
405 illumination by using a white light-emitting diode (LED) array with an intensity of 100
406 mW cm⁻² in a nitrogen atmosphere at about 40°C. **d**, The MPPT curve of an encapsulated
407 NBG-containing PSC with YbO_x held at 85°C under 1-sun illumination and 50% relative
408 humidity in ambient air (ISOS-L-3 conditions). The light source is a white light LED solar
409 simulator with a simulated AM 1.5G spectrum. The temperature was controlled and
410 monitored by polyimide heating film with a digital-displayed temperature controller. **e-g**,
411 Evolutions of Pb 4f, I 3d, and Yb 4d XPS peaks of the perovskite/YbO_x bilayers as a
412 function of the storage period in a nitrogen-filled glovebox. The perovskite film without
413 the YbO_x is marked as “control”, and the perovskite/YbO_x bilayer is marked as “target.”

414 **Methods**

415 **Materials.** Lead diiodide (PbI₂, 99%), lead dibromide (PbBr₂, 99%), [2-(3,6-dimethoxy-
416 9H-carbazol-9-yl)ethyl]phosphonic Acid (MeO-2PACz) and [2-(9H-Carbazol-9-

417 yl)ethyl]phosphonic Acid (2PACz) were purchased from Tokyo Chemical Industry Co.,
418 Ltd (TCI, Japan). Formamidinium iodide (FAI), methylammonium iodide (MAI), and
419 methylammonium bromide (MABr) were purchased from Greatcell Solar. Rubidium
420 iodide (RbI, >99.99%) was purchased from Alfa Aesar. Cesium iodide (CsI, >99.99%) and
421 1-butyl-1-methylpiperidinium tetrafluoroborate ([BMP]⁺[BF₄]⁻, 99%) were purchased
422 from Sigma Aldrich (USA). [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was
423 purchased from Nano-C Tech. (USA). Poly [bis (4-phenyl) (2, 4, 6-trimethylphenyl) amine]
424 (PTAA, M_w~13,000) and phenylethylammonium iodide (PEAI) were purchased from
425 Xi'an Polymer Light Technology Corp (China). Nickel oxide (NiO_x) nanoparticles, C₆₀,
426 and bathocuproine (BCP) were purchased from Advanced Election Technology Co., Ltd
427 (China). Ytterbium (99.9%) was purchased from Kurt Lesker (Shanghai) Trading
428 Company Inc. Magnesium fluoride (MgF₂, 99.99%) was purchased from Alfa Aesar. Ultra-
429 dry dimethylformamide (DMF), ultra-dry dimethyl sulfoxide (DMSO), ultra-dry
430 isopropanol (IPA), ultra-dry ethanol, ultra-dry anisole, and ultra-dry chlorobenzene (CB)
431 were purchased from commercial sources (Acros). Toluene was purchased from
432 Sinopharm Chemical Reagent Co., Ltd (China). Copper (Cu) was purchased from a
433 commercial source with high purity. All reagents were used as received without further
434 purification.

435 **Perovskite precursor solution.** The perovskite composition in the narrow-bandgap (NBG)
436 perovskite is $\text{Rb}_{0.05}\text{Cs}_{0.05}\text{MA}_{0.05}\text{FA}_{0.85}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$. The perovskite precursor solution
437 was prepared by mixing CsI (19.5 mg), RbI (15.9 mg), MABr (8.4 mg), FAI (219.5 mg),
438 PbI_2 (656.9 mg), and PbBr_2 (27.5 mg) in 1 mL mixed solvent of DMF:DMSO (4/1, v/v)
439 and the resulting precursor solution was stirred at 50°C for 2 h before use³. For the mid-
440 bandgap (MBG) perovskite, the perovskite composition is
441 $(\text{Cs}_{0.05}\text{FA}_{0.85}\text{MA}_{0.10})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$. The perovskite precursor solution was prepared by
442 mixing PbI_2 (1.28 M), FAI (1.21 M), MABr (0.16 M), PbBr_2 (0.22 M), and CsI (0.07 M)
443 in a mixed solvent of DMF/DMSO (4/1, v/v), and the resulting precursor solution was
444 stirred at 70°C for 2 h before use. For the wide-bandgap (WBG) perovskite, the perovskite
445 composition is $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$. The perovskite precursor solution was prepared
446 by mixing PbI_2 (0.56 M), FAI (1.16 M), PbBr_2 (0.84 M), and CsI (0.24 M) in a mixed
447 solvent of DMF/DMSO (4/1, v/v), and the resulting precursor solution was stirred at 50°C
448 for 5 h before use.

449 **Device fabrication.** Before device fabrication, the pre-patterned ITO or FTO substrates
450 were ultrasonically cleaned using an aqueous detergent solution, deionized water, acetone,
451 and IPA for 20 min. Subsequently, the as-cleaned ITO and FTO substrates were treated
452 with UV-ozone for 10 min.

453 For the WBG perovskite, 15 mg mL⁻¹ NiO_x nanoparticle in a mixed solvent of IPA:
454 deionized water (1:3) solution was spin-coated onto ITO substrates at 3,000 r.p.m. for 30 s
455 (with a ramping rate of 1,000 r.p.m. s⁻¹), and the as-formed films were heated at 150°C for
456 30 min in ambient air. The subsequent overlayers were deposited after the substrates cooled
457 down to room temperature. The following operations were all carried out in an N₂-filled
458 glovebox (with H₂O and O₂ concentrations of < 0.1 ppm). Before depositing the perovskite
459 layer, the NiO_x film was modified by the self-assembling monolayer of 2PACz and MeO-
460 2PACz. The solutions of 2PACz and MeO-2PACz with the same concentration (0.5 mg
461 mL⁻¹ in ethanol) were mixed with the volume ratio of 1:1, and then the mixed solution of
462 2PACz and MeO-2PACz was spin-coated onto the NiO_x film at 3,000 r.p.m. (with a
463 ramping rate of 1,000 r.p.m. s⁻¹) for 30 s followed by annealing at 100°C for 5 min. When
464 the films cooled down to room temperature, the perovskite precursor solution was
465 deposited onto the substrates by a consecutive two-step program at 1,000 rpm for 10 s with
466 a ramping rate of 1,000 r.p.m. s⁻¹ and 5,000 r.p.m. for 35 s with a ramping rate of 1000
467 r.p.m. s⁻¹. During the second step, 300-μL of anisole doped with the ionic liquid
468 ([BMP]⁺[BF₄]⁻, 0.01 mg mL⁻¹) was poured on the center of the spinning substrates at 5 s
469 before the end of the whole program. Then the samples were immediately transferred to
470 the hotplate, annealing at 100°C for 30 min. For the post-treatment of the WBG perovskite
471 films, 200-μL of PEAI (5 mg mL⁻¹ in IPA) and 100-μL of MAI (5 mg mL⁻¹ in IPA) were
472 mixed in 705-μL of a mixed solvent of DMF/IPA (5/700, v/v) to obtain 1,005-μL of post-

473 treatment solution. Then 50- μL of post-treatment solution was dynamically spin-coated on
474 top of the perovskite film, followed by annealing at 100°C for 5 min.

475 For the MBG perovskite, 2 mg mL^{-1} PTAA (in toluene) solution was spin-coated onto ITO
476 substrates at 5,000 r.p.m. for 30 s (with a ramping rate of 2,500 r.p.m. s^{-1}), and as-formed
477 films were heated at 120°C for 10 min. The subsequent overlayers were deposited after the
478 substrates cooled down to room temperature. Then, the PEAI solution (10 mg mL^{-1} in IPA)
479 was spin-coated onto the PTAA-coated substrates at 5,000 r.p.m. for 30 s (with a ramping
480 rate of 2,500 r.p.m. s^{-1}), and then the samples were heated at 100°C for 5 min. Subsequently,
481 the perovskite films were spin-coated onto the substrates by a two-step program at 2,000
482 r.p.m. for 10 s (with a ramping rate of 200 r.p.m. s^{-1}) and 6,000 r.p.m. for 30 s (with a
483 ramping rate of 1,000 r.p.m. s^{-1}), respectively. During the second step, 100- μL of CB was
484 poured on the center of the spinning substrates at 16 s before the end of the whole program.
485 Then the samples were immediately transferred to the hotplate, annealing at 105°C for 30
486 min.

487 For the NBG perovskite, the MeO-2PACz (0.5 mg mL^{-1} , in ethanol) solution was spin-
488 coated onto the pre-cleaned FTO substrates at 3,000 r.p.m. for 30 s and annealed at 100°C
489 for 10 min in an N_2 -filled glove box. The perovskite films were prepared according to the
490 previous work reported elsewhere³.

491 The samples were then transferred to a vacuum chamber to make the charge-selective layer
492 without air exposure. C₆₀ (35 nm) was thermally evaporated in a vacuum chamber with a
493 base pressure of $< 4 \times 10^{-4}$ Pa. For the NBG perovskites, the PCBM solution (20 mg mL⁻¹
494 in CB) was spin-coated on top of the perovskite layer at the speed of 1,000 r.p.m. for 30 s
495 (with a ramping rate of 200 r.p.m. s⁻¹).

496 For the buffer layer fabrication, the samples were transferred to a separate vacuum chamber
497 with a base pressure of $< 4 \times 10^{-4}$ Pa. The ytterbium oxide (YbO_x) buffer layer with a
498 thickness of 1.5 nm was obtained by the thermally evaporated metal ytterbium (Yb) in the
499 vacuum chamber. The thermal evaporation rate for the metal ytterbium is 1 Å/s. Note that
500 Yb will be naturally oxidized into the YbO_x in a few minutes without intentional additional
501 oxidation processes. For the control devices with the BCP interlayer, BCP (1 mg mL⁻¹ in
502 ethanol) was spin-coated at 5,000 r.p.m. with a ramping rate of 2,500 r.p.m. s⁻¹ for 30 s.

503 Finally, a 100-nm thick Cu electrode was thermally evaporated on the samples in the
504 vacuum chamber ($< 4 \times 10^{-4}$ Pa) through a metal shadow mask with an aperture area of 10.3
505 mm². The aperture mask area for the photovoltaic performance tests is 7.2 mm². Besides,
506 for the WBG and MBG devices, MgF₂ (100 nm) was deposited on the glass side of the ITO
507 substrate as the anti-reflection coating, while for the NBG devices, MgF₂ (125 nm) was
508 deposited on the glass side of the FTO substrate.

509 **Stability assessment.** For the stabilized power output (SPO) test, the encapsulated devices
510 were measured at the maximum power point (MPP) under full-spectrum white LED
511 illumination (continuous 1-sun illumination) in ambient air or in the N₂ atmosphere.
512 Thermal stability assessments for encapsulated devices were conducted by storing the
513 encapsulated PSCs on a hot plate at 85°C in an N₂ atmosphere. Photovoltaic performances
514 were regularly measured when cooled down to room temperature. For the NBG-containing
515 PSCs, the PCBM electron transport layer was replaced by C₆₀ (35 nm, prepared by thermal
516 evaporation) in the thermal stability and long-term MPP tracking assessments. The
517 encapsulation for the device was done by capping the device with a glass slide, using UV
518 adhesive as the sealant. The encapsulation process was finished in an N₂-filled glovebox
519 (with H₂O and O₂ concentrations of < 0.1 ppm). For the stability test under the ISOS-L-3
520 protocol, the temperature was controlled and monitored by the polyimide heating film with
521 a digital display in temperature control. The ageing devices adhered to the polyimide
522 heating film.

523 **PV characterization.** The PSCs' current density–voltage (*J–V*) characteristics were
524 performed using a Keithley 2400 Source Meter under AM 1.5G illumination with a Xenon-
525 lamp solar simulator (XES-40S1, SAN-EI). Before the measurement, the light intensity of
526 100 mW cm⁻² was calibrated using a standard monocrystalline silicon solar cell with a KG-
527 5 filter. The external quantum efficiency (EQE) was measured by a QE-R3011

528 measurement system (Enli Technology, Inc.). Electroluminescence (EL) quantum
529 efficiency (EQE_{EL}) was carried out at room temperature (297 K) in an N_2 -filled glovebox.
530 A Keithley 2400 Source Meter and an integration sphere (CME-LP38) coupled with a
531 spectrometer (Flame, Ocean Optics) were used for the measurements. The device was
532 placed on top of the integration sphere, and only forward light emission can be collected.
533 The devices were swept from zero bias to forward bias.

534 **Film characterization.** The field-emission scanning electron microscope (FE-SEM) was
535 used to investigate the top-view and cross-sectional morphology with an accelerating
536 voltage of 10 kV (Hitachi U8010). Spin-coating perovskite films on the ITO-coated glass
537 substrates prepared samples for Ultraviolet-visible (UV-vis) absorption spectra
538 characterizations. Then their UV-vis absorption spectra (350-850 nm) were recorded by a
539 spectrophotometer (UH4150, Hitachi, Japan) with the background noise subtracted before
540 testing. During the measuring process, the perovskite films were exposed to air for less
541 than 5 min. The time-resolved photoluminescence (TRPL) spectroscopy measurements
542 were performed by an Edinburgh Instruments FLS1000 photoluminescence spectrometer
543 (Edinburg, UK), and a pulsed laser measured all TRPL-related tests with the excitation
544 wavelength of 450 nm after 120-second illumination. Temperature-dependent current
545 density–voltage (J – V) characteristics of $\text{ITO}/[\text{YbO}_x (5 \text{ nm})/\text{Cu} (1 \text{ nm})]_{20}/\text{Cu}$ and
546 $\text{ITO}/[\text{YbO}_x (2 \text{ nm})]_{20}/\text{Cu}$ were measured by using HP4140B picoammeter dominated by

547 computer within a cryostat. Both devices processed by evaporating 20 alternative layers.
548 For $[\text{YbO}_x (5 \text{ nm})/\text{Cu} (1 \text{ nm})]_{20}$, we mean we have deposited 20 alternating layers of 5 nm
549 YbO_x followed by 1 nm Cu. The starting low temperature is 80 K cooled with liquid
550 nitrogen, and data was acquired by every 30 K increase controlled by MercuryiTC low
551 temperature environment controller. Grazing incidence wide-angle X-ray scattering
552 (GIWAXS) measurements for amorphous Yb films deposited on various substrates were
553 conducted at the BL17B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF).
554 The X-ray wavelength was 1.240 Å with a grazing incident angle of 1.0 degree, and the
555 scattering intensity was detected by a PILATUS 2M detector.

556 Thermo Scientific ESCALAB Xi⁺ system was used to acquire the X-ray photoelectron
557 spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and the reflection
558 electron energy loss spectroscopy (REELS) spectra. All samples were transferred into the
559 analysis chamber via a vacuum transfer module avoiding exposure to the air. Unless
560 otherwise stated, the gas cluster ion beam (GCIB) sputtering technology carried out the
561 depth profiles with the parameters of 2000-cluster sizes at 4 keV ion energy. Ar⁺ ion
562 sputtering was used as a supplement to etch the hard materials, such as metal electrodes.

563 High-resolution transmission electron microscopy (HRTEM) and annular dark-field
564 scanning transmission electron microscopy (ADF-STEM) images have been obtained by
565 using a JEM-2100F field emission gun microscope with a 0.19 nm point-to-point resolution

566 at 200 kV equipped with Energy disperse X-ray (EDX) detectors. Images have been
567 analysed using Gatan Digital Micrograph software. To reduce the electron dose during the
568 HRTEM characterization, we limited the total electron beam exposure time to within 5 s.
569 All the time-of-flight secondary-ion mass spectrometry (TOF-SIMS) profiles were
570 acquired by a PHI TRIFT V nanoTOF (ULVAC-PHI, Japan) system using slice-and-view
571 analysis scheme. A 20 kV C_{60}^+ beam with a pulse frequency of 8200 Hz and a pulse length
572 of 15 ns was used as the primary-ion beam. All the secondary-ion signals were acquired
573 from a $50\ \mu\text{m} \times 50\ \mu\text{m}$ area. A 1 kV Ar^+ beam was used as the sputter source to remove the
574 surface material during TOF-SIMS profiling, and the sputtering crater size was $1000\ \mu\text{m} \times$
575 $1000\ \mu\text{m}$. All the secondary-ion data presented in the profiles were normalized by total ion
576 intensities.

577 **Data and materials availability**

578 All data are available in the main text or the supplementary materials, and are also available
579 from the corresponding author on reasonable request

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595 **Author contributions**

596 D.L., Z.-H.L., P.C., Y.X., and R.Z. conceived the idea and designed the experiments. P.C.,
597 Y.X., S.L. X.J., and T.H. fabricated PSCs and characterized photovoltaic performances.
598 P.C. and M.Y. performed electroluminescence tests. Y.X., P.K., and Pietro. C. contributed
599 to the analysis of electroluminescence results. X.L. conducted EQE measurements. J.H.,
600 J.W., Y.S., and P.T. conducted the TEM and EDX tests. J.H. and N.C. performed REELS,
601 UPS, and XPS measurements. J.H., N.C., D.W., D.L., R.S., and Z.-H.L. contributed to
602 analyzing REELS, UPS, and XPS results. N.C. and Z-H.L. contributed to the analysis of
603 charge transport mechanisms. J.H., P.C., Y.X., and Q.L. conducted the SEM

604 measurements. S.L. and L.Z. helped perform the GIWAXS measurements. P.C. and Y.X.
605 measured UV-Vis light absorption. C.-H.H., Y-W.Y., and J.-J.S. performed TOF-SIMS
606 measurements. P.C., Y.X, and Q.Z. performed the TRPL test and did data analysis. H.Y.,
607 Y.X., and P.C. conducted the stability test. D.L., Q.G., Z.-H.L., H.J.S., and R.Z. directed
608 and supervised the project. P.C. and Y.X. wrote the first draft of the paper. D.L., Q.G., Z.-
609 H.L., H.J.S., and R.Z. revised the paper. All authors analyzed their data, reviewed and
610 commented on the paper.

611 **Conflict of interest**

612 Henry J. Snaith is the founder and Chief Scientific Officer of Oxford Photovoltaics, a
613 company commercializing perovskite photovoltaics.

614 **Extended data figure legends**

615 **Extended Data Fig. 1 | Overview of buffer layers.** **a**, Schematic illustration of the
616 functions of an ideal buffer layer between the electron-selective layer (ESL) and the metal
617 electrode, showing suppression of the harmful species movement and the non-radiative
618 recombination. **b**, Standard molar Gibbs free energy ($\Delta_f G$) of formation at 298.15 K in kJ
619 mol⁻¹ of representative metal oxides including ZnO, SnO₂, ZnSnO₄, TiO₂, Cr₂O₃, and
620 Yb₂O₃. **c**, Schematic illustration of the thermal evaporation deposition process of the metal
621 Yb.

622 **Extended Data Fig. 2 | XPS characterizations. a**, Photograph of 1.5 nm YbO_x film
623 deposited on a large-scale ITO substrate (100 cm²) by a scalable thermal evaporation
624 approach. The areas at the corner of the sample highlighted by the dotted box were used to
625 conduct the XPS measurements. **b**, Yb 4d XPS spectra corresponding to the highlighted
626 areas in (a). The XPS data show that YbO_x on an 100-cm² substrate can be formed when
627 upscaling in the device fabrication chamber with a base pressure of 10⁻⁴ Pa.

628 **Extended Data Fig. 3 | XPS measurements and photographs of Yb bulk and YbO_x**
629 **surface. a**, Yb 4d XPS spectrum of the Yb bulk with 2400 s Ar ion etching. Photographs
630 of the pristine Yb bulk with a naturally oxidized YbO_x surface (b) and the polished Yb bulk
631 (c) in ambient air. The color change indicates that the refreshed metal Yb surface would
632 quickly react with oxygen upon oxygen exposure, forming YbO_x on the surface.

633 **Extended Data Fig. 4 | The oxidization process of Yb. a**, Yb 4d XPS spectrum of an as-
634 prepared ITO/YbO_x (1.5 nm) film. The sample was immediately transferred from the
635 physical vapor deposition system to the XPS chamber by the vacuum transfer module
636 without exposure to the air. **b**, Yb 4d XPS spectra of a clean Yb⁰ surface spontaneously
637 oxidized in the UHV XPS chamber. L represents Langmuir. **c**, The YbO_x thickness and
638 Yb³⁺/Yb⁰ ratios as a function of the exposure dose. **d-i**, Yb 4d XPS spectra with increased
639 exposure dose.

640 **Extended Data Fig. 5 | Transmission electron microscopy (TEM) measurements. a, b,**
641 TEM images of YbO_x directly deposited on the carbon-supported copper (50 and 20 nm).
642 **c,** The typical fast Fourier transform (FFT) spectrum (30 × 30 nm² area) indicates the
643 amorphous crystal structure of YbO_x.

644 **Extended Data Fig. 6 | 2D grazing incidence wide-angle X-ray scattering (GIWAXS)**
645 **measurements.** The 2D GIWAXS patterns at an incidence angle of 1.0° for YbO_x films
646 prepared on different substrates including silicon (**a**), glass (**b**), and ITO-coated glass (**c**),
647 respectively. The thickness of the deposited YbO_x film for this measurement is 10 nm. **d,**
648 The 2D GIWAXS pattern of the pristine ITO-coated glass.

649 **Extended Data Fig. 7 | Gap states in the YbO_x film and charge-carrier transport**
650 **measurements. a,** Yb 4d XPS spectra of the YbO_x film with a thickness of 40 nm. **b,**
651 Valence band spectra of YbO_x. There exists a considerable density of gap states below the
652 Fermi level. **c,** Current density–voltage characteristics of the ITO/[YbO_x (2 nm)]₂₀/Cu over
653 temperature ranged from 120 K to 300 K. Note that the 40 nm YbO_x deposition is
654 completed by evaporating 20 alternative layers. **d,** The plot of conductivity against
655 temperature. The conductivity is calculated at 26 mA cm⁻², where the injected current is
656 equal to the short-circuit current of a narrow-bandgap PSC under 1-sun illumination. Note
657 that the pre-factor $\sigma_0 = (2.22 \pm 0.47) \times 10^{-3} \text{ S m}^{-1}$, and the characteristic parameter $B =$
658 10.33 ± 0.81 .

659 **Extended Data Fig. 8 | Charge-carrier transport measurements.** **a**, Current
660 density–voltage characteristics of the device with a configuration of ITO/[YbO_x (5 nm)/Cu
661 (1 nm)]₂₀/Cu over temperature ranged from 110 K to 290 K. **b**, The plot of conductivity
662 against temperature.

663 **Extended Data Fig. 9 | Time-of-flight secondary ion mass spectrometry (TOF-SIMS)**
664 **measurements.** TOF-SIMS depth profiles of the BCP- or YbO_x-based PSCs with and
665 without ageing. **a**, **c**, are the control (with the BCP buffer layer) and target device (with the
666 YbO_x buffer layer), respectively. **b**, **d**, are TOF-SIMS profiles of both control and target
667 devices after ageing at 85°C for 200 h in the N₂ atmosphere, respectively. The highlighted
668 secondary ion distribution: 1: Cs⁺; 2: Rb⁺; 3: Cu⁺, 4: I⁺; 5: Br⁺.

669 **Extended Data Table 1 | Photovoltaic parameters.** Summary of photovoltaic
670 parameters for the champion p-i-n PSCs with NBG (1.54 eV), MBG (1.59 eV), and WBG
671 perovskites (1.77 eV). The devices were measured from reverse scans (RS) under simulated
672 AM 1.5G solar irradiation at 100 mW cm⁻². For p-i-n PSCs with WBG perovskites, RS is
673 from 1.35 V to -0.02 V. For p-i-n PSCs with NBG and MBG perovskites, RS is from 1.22
674 V to -0.02 V).

675 ^aThe average device parameters and standard deviations are based on 15 devices.







