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Double-side 2-dimensional/3-dimensional heterojunctions for inverted perovskite solar cells

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Abstract

Defects at the top and bottom interfaces of three-dimensional (3D) perovskite photo-absorbers diminish the performance and operational stability of perovskite solar cells (PSCs) due to charge recombination, ion migration, and electric-field inhomogeneities.[1-5] Here, we demonstrate that long alkyl-amine ligands can generate near-phase pure two-dimensional (2D) perovskites at the top and bottom 3D perovskite interfaces and effectively resolves these issues. At the rear-contact side, we find that the employed alkyl-amine ligand strengthens the interactions with the substrate through acid-base reactions with the phosphonic acid group from the employed organic hole-transporting self-assembled monolayer molecule, thus regulating the 2D perovskite formation. With this, inverted PSCs with double-side 2D/3D heterojunctions achieved a power conversion efficiency (PCE) of 25.6% (certified 25.0%), retaining 95% of their initial PCE after 1000 hours of 1-sun illumination at 85 degrees Celsius in air.

32 **Main**

33   Engineering of perovskite interfaces is essential to enhance the performance and stability of

34   perovskite solar cells (PSCs). Two-/three-dimensional (2D/3D) perovskite heterojunctions have

35   shown particular promise towards this end.[6-16] Usually, such heterojunctions are formed by post-

36   treating an as-deposited 3D perovskite film with a solution that contains 2D ligands to reconstruct

37   through cation exchange the 3D perovskite surface into a 2D perovskite.[7-9,12,14] However, this

38   strategy is only applicable at the top surface of 3D perovskite films. Moreover, it usually results

39   in a 2D perovskite consisting of a mixture of multiple dimensionalities such as $n = 1, 2, 3$, *etc*. with

40   random crystal orientations, where n refers to the number of subsequent corner-sharing octahedral

41    $[PbI_6]^{4-}$ inorganic slabs.[8,12,14] Unfortunately, such mixed dimensionality may induce interfacial

42   energetic inhomogeneity and could impede charge transfer through band misalignment when such

43   a 2D/3D heterojunction is integrated into a charge-selective contact stack.[7,8,12,14] In contrast, phase-

44   pure 2D perovskite passivation can substantially reduce the charge-trap density and ion migration,

45   leading to significantly improved device performance and stability.[10,11] Hence, it is imperative to

46   narrow the distribution of the different n layers in 2D perovskites.[10,11,16] Yet, achieving phase-pure

47   2D perovskite passivating contacts with a proper crystal orientation is experimentally

48   challenging.[10,11,16]

49   Integrating 2D/3D heterojunctions at the buried bottom interface is desirable too, but has rarely

50   been reported to date.[17-19] The primary difficulty here is to avoid the dissolution of the pre-

51   deposited 2D layer or the organic ammonium-based ligands during the subsequent 3D perovskite

52   deposition.[17-19] Indeed, most organic ammonium ligands are readily dissolved into the highly polar

53   aprotic solvents typically used in 3D perovskite precursor inks such as dimethyl formamide (DMF)

54   and dimethyl sulfoxide (DMSO).[11,20,21] Hence, one approach for minimizing the dissolution of 2D

55   ligands during perovskite solution casting is to strengthen their interaction with the substrate. This

56   allows for immobilizing 2D ligands prior to perovskite deposition, and forming a 2D perovskite

57   underneath the 3D perovskite film through cation exchange and intercalation of the 2D ligands

58   into the perovskite film, post deposition.

59   **2D/3D heterojunction at the bottom interface**

60   We developed inverted (*p*–*i*–*n*) PSCs with a hole-collecting contact (*p*–type) that is formed by

61   anchoring 2PACz, a self-assembled monolayer (SAM), onto the transparent bottom electrode,

62 consisting of indium-tin oxide (ITO). To resolve the challenge of 2D/3D heterojunction formation

63 at the bottom of the perovskite film, we mixed the HBzA ligand into the 2PACz SAM solution,

64 which was then coated onto the ITO bottom electrode. Here, we hypothesized that the amine head

65 of the HBzA molecule would react with the phosphonic acid ($-PO(OH)_2$) group of the 2PACz,

66 forming an ionic bond, resilient against subsequent processing. This acid-base reaction is favorable

67 with the lower values of the negative log of the acid dissociation constant for the first proton (pK_{a1})

68 of the phosphonic acid (~2.5) and the negative log of the base dissociation constant (pK_b) of alkyl-

69 amines (~3.6).[22,23] We note that only the first proton transfer is favorable between 2PACz and

70 HBzA, owing to a higher pK_{a2} value of the second proton (~8.5).[22] We experimentally verified that

71 the abovementioned reaction takes place in the mixture of 2PACz and HBzA, as discussed in

72 **Extended Data Fig. 1a–b**. Moreover, the –OH group from HBzA can form hydrogen bonds with

73 $-PO(OH)_2$ and ITO, thus strengthening the attachment further.[24] The detailed explanation of all

74 these mechanisms is in **Fig. 1a**.

75 We then investigated the chemical properties of HBzA and 2PACz molecules on ITO using X-ray

76 photoelectron spectroscopy (XPS). The high-resolution spectrum of the carbon region (C1s) of

77 HBzA shows the presence of C=C, C–N, and C–OH bonds that correspond to the aromatic ring,

78 amine head, and the phenol group of HBzA, respectively (**Extended Data Fig. 1c**). Further, C1s

79 spectra of 2PACz feature the signature of C–P bonds, corresponding to its $-PO(OH)_2$ group. These

80 identical features of 2PACz and HBzA were also found after their mixture was coated on ITO,

81 indicating the presence of both molecules. To strengthen our hypothesis, we also did a washing

82 test on the ITO/HBzA and ITO/(HBzA+2PACz) samples with a highly polar aprotic DMF/DMSO

83 solvent mixture that can easily solvate HBzA molecules by forming strong hydrogen bonding. We

84 observed that if only HBzA layers are anchored on ITO, they could be easily washed away.

85 However, the presence of 2PACz significantly enhances the attachment of HBzA onto the ITO

86 surface, as indicated by a qualitative analysis of the marginal reduction of the atomic ratio of

87 nitrogen to indium (N/In) after washing (**Supplementary Table 1**). This supports our hypothesis

88 that HBzA and 2PACz form an ionic bonding through proton transfer from phosphonic acid to the

89 amine group. This bonding facilitates their adherence to the substrate during perovskite processing

90 and assists in the formation of a 2D perovskite layer beneath the 3D perovskite layer.

3

91 After successfully attaching HBzA ligands on the ITO/2PACz surface, we deposited the 3D

92 perovskite ink via spin-coating. The HBzA ligands are liberated after 3D perovskite deposition,

93 initiating the 2D perovskite formation at the bottom interface through cation exchanges between

94 $HBzA^+$ and formamidinium (FA^+) or caesium (Cs^+) of the 3D perovskite ink. This cation exchange

95 process is completed during the thermal annealing of perovskite films at 120 °C for 30 min to

96 crystallize the 2D/3D perovskite film. To prove this mechanism, we completely removed the

97 resulting perovskite layers from the ITO/2PACz/2D-HBzA/3D-perovskite structure by washing

98 the samples with a DMF/DMSO solution and measured the work function (WF) of the resulting

99 structure using kelvin-probe-force microscopy (KPFM). We noted that the WF of bare

100 ITO/(2PACz+HBzA) sample remained similar before and after washing with DMF/DMSO (5.08

101 eV, **Extended Data Fig. 2a–c**). However, after the perovskite film deposition and subsequent

102 removal of the HBzA ligands, the WF of ITO/(2PACz+HBzA) is shifted to 5.42 eV, closer to the

103 WF of pristine ITO/2PACz (5.40 eV) with identical conditions (**Extended Data Fig. 2d–e**). This

104 indicates that DMF/DMSO alone was not sufficient to remove HBzA molecules. Rather, the

105 removal was facilitated by the 3D perovskite deposition, corroborating our hypothesis that 2D

106 ligands are released only after perovskite film formation.

107 The cross-sectional high-resolution scanning transmission electron microscopy (HR-STEM)

108 images in **Fig. 1b** reveal the formation of a discontinuous 2D perovskite layer at the bottom

109 interface between ITO/2PACz and 3D perovskite layers. The discontinuity of 2D perovskite layers

110 might be related to their complex formation mechanism, such as random distribution of HBzA

111 molecules and their release during cation exchange. We further analyzed the 2D/3D perovskite

112 heterojunction at the bottom-side interface by photoluminescence (PL) spectroscopy and observed

113 distinct PL emission peaks for 2D perovskite at ~570 nm and ~520 nm corresponding to $n = 2$ and

114 $n = 1$, respectively (**Fig. 1c**).[12] The significantly high PL emission intensity of $n = 2$ indicates the

115 dominant formation of near-phase pure 2D perovskite layers. In addition, we performed PL

116 mapping at ~570 nm with different concentrations of HBzA ligand and observed discontinuities

117 for 2D perovskite crystal PL emission at the bottom interface (**Supplementary Fig. 1**), in

118 accordance with HR-STEM results.

119 We further analyzed the structural properties and chemical composition of 2D perovskite at the

120 bottom-side interface by gently separating the bottom-side 2D/3D perovskite film from the

121 ITO/hole-selective surface using the lift-off technique following previous report.[25] This approach

4

122 preserves the chemical and structural integrity of the film (see the schematics of the process in
123 **Supplementary Fig. 2a**). We then characterized the bottom-side perovskite film by scanning
124 electron microscopy (SEM) and XPS measurements. SEM top-view images of the lift-off samples
125 show no distinctive morphological damage to the control and 2D/3D heterojunction samples
126 (**Supplementary Fig. 2b**). However, we note that the crystal grain-sizes of perovskite of 2D/3D
127 samples are larger (1.64 ± 0.31 μm) compared to control perovskite (0.93 ± 0.20 μm), indicating
128 that 2D perovskite formation at the bottom interface also regulates the crystallization of the
129 overlying 3D perovskite film.[26] Further, the XPS analysis of 2D/3D samples revealed the presence
130 of C–O and C–N bonds at 286.5 and 285.6 eV, associated with HBzA ligands (**Supplementary
131 Fig. 2c**).

132

133 **3D/2D heterojunction at the top interface**

134 For the 3D/2D heterojunction at the top interface, we developed a simple two-step hybrid method
135 to form phase-pure 2D perovskite layers. This process initially involves depositing the PbI$_2$ layer
136 with controlled thickness via vacuum evaporation on top of the as-prepared 3D perovskite film
137 (see **Fig. 2a**, step (i)). This is then followed by dropping the HBzA salt or mixture of HBzA
138 salt+FAI solutions on top of perovskite/PbI$_2$ film in step (ii). Finally, the samples are thermally
139 annealed to form a 2D perovskite layer with controllable dimensionality and phase purity in step
140 (iii).

141 **Fig. 2b** shows the normalized PL spectra of 3D/2D perovskite films for two conditions. First, when
142 coating the HBzA salt cation-only solution, the 3D/2D perovskite sample shows a single emission
143 peak at a low wavelength ~520 nm (corresponding to $n = 1$).[8,12,27] Second, the sample based on the
144 mixture of HBzA salt+FAI also shows a single emission peak but at a higher wavelength (~570
145 nm), which corresponds to $n = 2$.[8,12] These results confirm the success of our method to control
146 the phase-purity and dimensionality of 2D perovskites, which to date remained a challenge.[7,8,12,14]
147 In contrast, the conventional method by direct coating of HBzA salt solution on top of 3D
148 perovskite followed only steps (ii) and (iii) (with the absence of PbI$_2$ deposition) forms a mixture
149 of multiple dimensionalities of 2D-perovskite ($n = 1$, 2, and 3; **Supplementary Fig. 3**), consistent
150 with previous works.[8,12] We note that a higher dimensionality of the 2D perovskite ($n > 1$)

151 passivation layer is critical, owing to a higher conductivity by having less bulky-organic cations

152 interfaces.[8,11,12]

153 Next, we identified the crystal orientation and dimensionality of the 2D perovskite layers through

154 grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. **Fig. 2c** shows the

155 diffraction map of GIWAXS of the 3D/2D sample with strong diffraction peaks at lower q_z (0.31

156 Å^{-1} and 0.64 Å^{-1}) representing the (002) and (004) planes of 2D perovskite ($n = 2$), respectively,

157 with a layer spacing d of ~20.3 Å^{-1} and ~9.8 Å^{-1}.[13,14,28,29] Interestingly, strong and more discrete

158 Bragg spots at a higher q_z (~1.5 Å^{-1} and ~1.7 Å^{-1}) were observed in the 3D/2D sample. This

159 indicates the improved orientation of the 2D perovskite corresponding to the (282), (121), and

160 (082) planes, formed with perpendicular orientation to the 3D perovskite underneath, as

161 highlighted with oval dot lines.[30,31] In contrast, we do not observe the diffraction peaks at lower q_z

162 and discrete Bragg spots in control perovskite samples (**Supplementary Fig. 4a–b**). This result is

163 also consistent with the X-ray diffraction pattern of phase-pure 2D perovskite thin film, as shown

164 in **Supplementary Fig. 4c–d**. Further, we visualize the 2D perovskite formation and orientation

165 at the top-contact using cross-sectional HR-STEM in **Fig. 2d**, with a predominantly perpendicular

166 orientation. In addition, a thin layer of 2D perovskite does not change the morphology of 3D

167 perovskite underneath (**Supplementary Fig. 5**), suggesting the robustness of our hybrid method

168 to form perovskite heterostructures.

169

170 **Device performance and characterizations**

171 After successfully completing the near-phase pure 2D perovskite passivation layers at the bottom

172 and top 3D perovskite interfaces, we adopted them to PSCs with a structure of ITO/2PACz/2D-

173 perovskite/3D-perovskite/2D-perovskite/C$_{60}$/BCP/Ag (**Fig. 3a**). We first tested various alkyl-

174 amine-based 2D ligands with different concentrations with respect to the ratio between 2PACz

175 SAM and 2D ligands at the bottom-side 2D/3D passivation, as shown from the statistical analysis

176 of devices performance in **Extended Data Fig. 3a–b**. The device results revealed that the optimum

177 concentration of the 2D ligand at the bottom contact is around a 1:1 molar ratio with 2PACz SAM.

178 The higher concentration of 2D ligand at the bottom interface leads to a thicker 2D perovskite

179 layer, lowering the FF of devices. This is likely due to the nature of higher resistance of long-alkyl

180 ligands in parallel orientation to the 3D perovskite layer, which can inhibit charge transport.[32]

181 Interestingly, among the five alkyl-amine ligands tested, the HBzA ligand gives the highest
182 performance, potentially due to the addition of an –OH group that could form a hydrogen bond
183 with –PO(OH)$_2$ and ITO or coordinate with 3D perovskite at the 2D/3D interface.[33,34] The longer
184 2D ligand (*i.e.*, hexylmethylamine) results in the lower performance, potentially due to a higher
185 charge transfer resistivity induced by long-alkyl ligand. This suggests the critical roles of
186 additional functional groups and the design of the proper size of 2D ligands for bottom
187 passivation.[8,16]

188 Next, we fabricated the top-side 3D/2D heterojunction using the abovementioned hybrid method.
189 Here, we deposited PbI$_2$ with different thicknesses (7, 15, and 25 nm) and found the thickness of
190 2D perovskite will depend on the initial thickness of the inorganic PbI$_2$ layer. Based on the device
191 results, it is found that 15 nm-thick PbI$_2$ film results in 35 nm-thick 2D perovskite layer, which is
192 optimal for top-side passivation (**Extended Data Fig. 3c**). In contrast, a 25 nm PbI$_2$ film forms
193 thicker 2D perovskite (around 55 nm, see cross-sectional SEM image in **Supplementary Fig. 6**),
194 which slows down the charge transfer/extraction rate at the perovskite/C$_{60}$ interface. It is consistent
195 with the decreased FF values from these devices, as indicated by the transient PL measurement
196 and differential lifetime analysis in **Supplementary Fig. 7**.

197 We then investigated the relation between the 2D perovskite orientation and charge transfer and
198 extraction rates. For this, we compared the charge transfer and extraction rates between the 3D
199 perovskite and C$_{60}$ when a 35 nm-thick 2D perovskite layer prepared by hybrid and solution post-
200 treatment methods is inserted between them. It should be noted that the 2D perovskite layer
201 prepared with solution post-treatment method has a parallel orientation to the 3D perovskite
202 surface, which significantly hinders charge transport, and limits the thickness of the 2D
203 layer.[8,11,12,16,35]

204 The charge transfer and extraction at the interfaces also depend on the energetic alignment between
205 3D perovskite and charge-selective contacts (**Extended Data Fig. 4a**). With the two-step hybrid
206 method, the secondary electron-cut-off of 2D perovskite shifted to lower binding energy
207 (**Extended Data Fig. 4b**). As a result, the conduction band minimum (CBM) of top-side phase-
208 pure 2D perovskite ($n = 2$) prepared by the hybrid method was deeper compared to the previously
209 reported mix-phase of 2D perovskite top-contact passivation using the conventional solution post-
210 treatment method, which resulted in dramatically minimizing the electron barrier.[8,12,16] Further,

211 the slightly deeper valence band maximum (VBM) of the bottom-side 2D perovskite compared to

212 the control 3D perovskite is favourable for hole transfer at the ITO/2PACz contact interface

213 (**Extended Data Fig. 4c–d**).

214 We then adopted double-side 2D/3D heterojunction passivation to our inverted PSCs and

215 demonstrated a maximum PCE of 25.63% (V_{OC} = 1.19 V, J_{SC} = 24.94 mA cm^{-2}, and FF = 85.9%,

216 see **Fig. 3b**) under reverse scan and stabilized PCE of 25.1% using triple-cation

217 $Cs_{0.025}MA_{0.075}FA_{0.90}PbI_3$ perovskite with a bandgap of 1.53 eV (**Supplementary Fig. 8**). This

218 result represents an absolute ~2.3% PCE enhancement compared to control devices (PCE around

219 23.3%) and >1% to only top- or only bottom-side 2D/3D heterojunction with PCE around 24%.[8,10-

220 12] **Fig. 3c** shows the statistical analysis results of the PCE, V_{OC}, and FF values from 25 devices for

221 each condition. We demonstrated the universality of our approach by testing various hole-

222 transporting SAM molecules (*i.e.*, 2PACz, MeO-2PACz, and 4PADCB) and other perovskite

223 compositions of $Cs_{0.05}FA_{0.95}PbI_3$ (~1.54 eV) with PCEs reaching up to 25% for each condition, as

224 shown from the statistical analysis of devices in **Supplementary Figs. 9** and **Extended Data Fig.**

225 **5,** respectively. We also confirmed the high process robustness of our approaches by showing less

226 than 1% PCE deviation from person-to-person, performed by three different researchers

227 (**Supplementary Fig. 10**). The performance of the double-side 2D/3D heterojunction passivated

228 solar cells were verified by an independently accredited testing center by presenting a PCE of

229 25.00% (V_{OC} = 1.17 V, J_{SC} = 25.00 mA cm^{-2}, and FF = 85.7% under reverse current-voltage scan,

230 **Supplementary Fig. 11**). This result represents one of the highest certified efficiencies in inverted

231 PSCs in current literature (**Supplementary Table 2**).

232 Notably, the $V_{OC} \times$ FF value of our double-side 2D/3D heterojunctions-based device was around

233 91% with respect to the Shockley–Queisser limit, one of the highest values among PSCs with only

234 top-side or bulk passivation (**Supplementary Fig. 12**). The high V_{OC} and FF values of the devices

235 can be associated with the low charge recombination and traps at the top and bottom interfaces.[15,36]

236 First, we measured the PL quantum yield (PLQY) to demonstrate the quality of perovskite film

237 before and after 2D perovskite passivation. The substantially improved PLQY of the double-side

238 2D/3D passivation (6.67% ± 0.58%) confirms the high quality of 2D/3D/2D perovskite film

239 compared to control perovskite sample (1.84% ± 0.63%) and one-side 2D/3D passivation sample

240 only (**Extended Data Fig. 6a**). Even after adding the C_{60} layer, the maintained a high PLQY value

241 of double-side 2D/3D perovskite (5.78% ± 0.33%) versus the control sample (significantly

242 dropped around $0.19\% \pm 0.06\%$), demonstrating the improved optoelectronic quality of perovskite

243 layer with the full stack of devices. This suggests that the 2D perovskite passivation layer can

244 efficiently suppress the charge recombination at these interfaces. These results are also consistent

245 with the longer Shockley-Read-Hall lifetime of double-side 2D/3D heterojunctions (2.69 μs),

246 around three and two times longer versus control (0.97 μs), and only one-side passivation (1.34 μs

247 and 1.73 μs for the bottom- and top-side only passivation, respectively), as shown in **Extended**

248 **Data Fig. 6b**.

249 We also determined the trap states for control and double-side 2D/3D passivation of perovskite

250 films using space-charge-limited-current (SCLC) and thermal admittance spectroscopy (TAS)

251 analyses.[12,37] For the SCLC, we fabricated the electron-only (ITO/SnO$_2$/perovskite/C$_{60}$/BCP/Ag)

252 and hole-only (ITO/SAM/perovskite/PTAA/MoO$_x$/Ag) devices to estimate the trap densities of

253 perovskite films. The trap-filled limited voltage (V_{TFL}) of double-side 2D/3D passivation samples

254 was more than 2-fold lower than control samples for both electron- and hole-only devices

255 (**Extended Data Fig. 6c–d**), indicating reduced trap density states (N_t) for both electron- and hole-

256 only devices (see **Supplementary Note 1**). This result suggests reduced negative and positive

257 defects at both interfaces with 2D perovskite passivation. It should be noted that the SCLC analysis

258 has limitations in extracting the exact value of N_t due to the presence of mobile ions in perovskite

259 materials.[38] Therefore, we also performed TAS analysis to quantify the N_t of perovskite films

260 relative to their energetic defect levels.[12,37] Overall, the N_t of double-side 2D/3D perovskite

261 passivation-based devices has lower N_t values in all energetic defect levels, suggesting sufficient

262 passivation of shallow and deep levels of defect in perovskite film by 2D perovskite passivation

263 (**Extended Data Fig. 6e**).

264 Further, the defects at the interfaces of perovskite films can affect to charge accumulation and

265 electric-field inhomogeneity of perovskite devices.[1,3-5,37] We then analyzed the capacitance–

266 voltage under various light illumination intensities to evaluate charge dynamics at the interfaces

267 (**Supplementary Fig. 13**). The shift in peak-potential (V_{peak}) under reverse bias with respect to the

268 illumination intensity reflected the degree of interfacial charge accumulation, which was due to

269 interfacial charge trapping.[37] Marginal shifting of the V_{peak} in the double-side 2D/3D device

270 indicated a reduced charge accumulation (less charge trapping) compared to the control device

271 (larger V_{peak} shifting), consistent with the above results. Interestingly, from the cross-sectional

272 KPFM mapping (**Fig. 3d and 3e**), stronger electric-field differences after 2D perovskite insertion

9

273 at the perovskite/C_{60} contact further prove a lower interfacial defect density.[39] We note that the

274 electric-field extended further into the perovskite film, more effectively repelling holes and thus

275 suppressing recombination at the perovskite/C_{60} interface.[40] We note that a similar electric-field

276 strength difference is observed at the 2PACz/perovskite contact for both control and double-side

277 passivation devices, presumably due to the higher dipole of 2PACz SAMs.[39] However, a uniform

278 electric-field is observed after 2D perovskite insertion at 2PACz/perovskite contact, as indicated

279 by a single peak. Consequently, this aids in charge transfer/extraction and leads to enhance V_{OC}

280 and FF values of devices.

281

282 **Stability and ion migration analyses**

283 We evaluated the long-term stability of encapsulated PSCs under light and thermal stresses. First,

284 **Fig. 3f** shows the stability under the open-circuit condition at 1-sun and 85 °C of the devices in air

285 (with a relative humidity of ~50%). The double-side 2D/3D heterojunction devices delivered a

286 relative PCE loss of only 5% after more than 1000 h. In contrast, the bottom- and top-side

287 passivation-based devices retain around 75% and 86% from their initial PCEs, respectively, versus

288 the control devices (without any 2D/3D heterojunction) retain around only 35% under identical

289 conditions. This result indicates the importance of passivating perovskite film's top and bottom

290 interfaces to improve their stability. Further, we measured the operational stability of double-side

291 2D/3D heterojunctions device under maximum-power-point tracking (MPPT). Around 90% of

292 their original PCE was retained after the PCE tracking for over 1000 h under 1-sun at 40 °C (**Fig.**

293 **3g**).

294 The degradation of perovskites under illumination and thermal stress can be related to defect-

295 induced ion migrations.[1,25,37,41] First, the defects related to iodine generation and migration were

296 investigated under 1-sun illumination at 85 °C. It has been reported that the significant release of

297 iodine compound from perovskite film during light soaking at elevated temperature is mainly due

298 to interstitial iodide or PbI_2 defects.[25,41] Passivating those defects by double-side 2D/3D

299 passivation suppresses the iodine generation/migration in perovskite films. This is proved by the

300 lowering intensity of UV-vis absorption spectrum of iodine at the maximum peak of wavelength

301 around 500 nm after immersing the perovskite films into toluene solution to light and heat

302 (**Extended Data Fig. 7a–b**).[25,41]

Finally, the activation energy for ion migration was obtained to reveal the ion-induced migration character in 2D/3D and control 3D perovskite films using temperature-dependent conductivity measurement.[37] The activation energy value of the control 3D perovskite was fitted to be 0.27 eV, in agreement with a previously reported value. In contrast, the activation energy value for the double-side 2D/3D heterojunctions film is increased to 0.47 eV (**Extended Data Fig. 7c**). This result indicates that the double-side 2D/3D heterojunctions have a significantly boosted energy barrier for ion migration, which might also improve the perovskite crystal stability.

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418

419 **Figure legends**

420 **Fig. 1: 2D/3D heterojunction at hole-selective bottom interface | a**, Scheme showing the
421 mechanism of 3D-perovskite formation on ITO/2PACz+HBzA and cation exchange at the bottom
422 interface (left-hand-side); 2D/3D heterojunction on ITO/2PACz bottom-contact (right-hand-side).
423 **b**, Cross-sectional High-angle annular dark-field (HAADF)-STEM image of near bottom HTL
424 contact with zoom-in of the area showing the parallel 2D perovskite layers. Fast Fourier transform
425 (FFT) shows 2D inter-planar spots (002) and (004) are matched with the dominant phase of $n = 2$.
426 **c**, Normalized PL spectra of bottom-side 2D/3D from low to high wavelengths with different
427 excitation directions from the glass-side and top perovskite surface film using 405 nm excitation.

428 **Fig. 2: 3D/2D heterojunction at electron-selective top interface | a**, Sketch explaining two-step
429 hybrid process to form 3D/2D heterojunction perovskites. **b**, Normalized PL spectra of each film
430 with light direction from the top perovskite surface film. **c**, GIWAXS maps of top-side 3D/2D
431 heterojunction at a low incidence angle (0.2°). **d**, Cross-sectional HAADF-STEM image of near
432 top C_{60}-contact with zoom-in of the area showing the perpendicular orientation of 2D-perovskite.

433 **Fig. 3: Device performance and stability analyses | a**, Sketch of the fabricated single-junction
434 PSC. **b**, Representative *J–V* curve for control, bottom, top, and double-side 2D/3D heterojunctions
435 PSC. **c**, Statistics parameters of PCE, V_{OC}, and FF (from top to bottom) values of PSCs. The box
436 and whisker plots indicate the statistical distribution: the center line represents the average value;
437 the bottom and top of the box represent the 25% to 75% percentiles; the small square represents
438 the mean; the whiskers represent outliers. **d, e**, Electric field distribution through both interfaces
439 from C_{60}-ETL to glass/ITO side acquired via KPFM cross-section scans. We mapped the photo-
440 voltage of the cells illuminated by an LED light. Note that we break the hole- and electron-selective
441 peaks for better visualization. **f**, Stability of encapsulated control bottom, top, and double-side
442 2D/3D passivation-based devices under 1-sun illumination at 85 °C and open-circuit conditions.
443 Five cells were used to construct the statistic, with the average represented by the symbol and the
444 standard deviation by the error bar. **g**, MPPT of an encapsulated double-side 2D/3D passivation-
445 based device under 1-sun illumination at 40 °C.

446

447 **Methods**

448 **Materials**

449 Dimethylformamide (DMF, 99.8%, anhydrous), dimethylsulfoxide (DMSO, 99.9%, anhydrous),
450 potassium chloride (KCl, 99.9%), 4-Hydroxybenzylamine (HBzA, C_7H_9NO), benzylamine,
451 phenethylamine, butylamine, hexylmethylamine, and cesium iodide (CsI, 99.9%) were all
452 purchased from Sigma Aldrich. Formamidinium iodide (FAI) and methylammonium chloride
453 (MACl) were purcahsed from Xian-Polymer. Lead iodide (PbI$_2$, ultra-dry) was purchased from

14

454 Alfa Aesar. 4-Hydroxybenzylammonium salts were purchased from Alfa-chemical. 2PACz ([2-

455 (9H-carbazol-9-yl)ethyl]phosphonic acid, >98.0%) and MeO-2PACz were purchased from TCI.

456 4PADCB (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid) was purchased from

457 Dyenamo. C_{60} (>99.5% purity) and bathocuproine (BCP, >99%) were purchased from Ossila Ltd.

Device fabrication

459 Glass/ITO substrates were washed in first acetone and then isopropyl alcohol for 20 min of each.

460 After washing, the substrates were dried and treated with UVO prior to use for 10-20 min. The

461 hole-transporting SAM (1 – 2 M) or mixed SAMs+2D-ligands (1:0.5, 1:1, 1:1.5, and 1:2 molar

462 ratio) were dissolved in ethanol. Then, the solution was spin-coated onto glass/ITO at 5000 rpm

463 for 30 s in a nitrogen-filled glovebox. After thermal annealing at 100 °C for 10 min, the hole-

464 selective layer coated ITO was cooled down and washed by ethanol by dynamic coating at 5000

465 rpm for 30 s to remove unbounded molecules.

466 A perovskite precursor solution (~1.5 M) of $Cs_{0.025}MA_{0.075}FA_{0.90}PbI_3$ was prepared by mixing FAI,

467 MAI, CsI, and PbI_2 with a molar ratio of 0.90:0.075:0.025:1 and then dissolving them in a mixed

468 solvent of DMF and DMSO (4:1 vol. ratio). 15 mol% of MACl was also added. For

469 $Cs_{0.05}FA_{0.95}PbI_3$ was prepared by mixing FAI, CsI, and PbI_2 with a molar ratio of 0.95:0.05:1 and

470 then dissolving them in a mixed solvent of DMF and DMSO (4:1 vol. ratio) to get ~1.5 M. Then,

471 around 10 mol% of MACl and 2 mol% of KCl were also added in the mixed perovskite solution.

472 The mixture of precursor solutions was shaken by a vortex shaker overnight at room temperature

473 until fully dissolved.

474 The perovskite precursor solution was spin-coated at 2000 rpm for 40 s and 6000 rpm for 10 s. At

475 the 10th s, 200 mL of anisole was dropped onto the films by the end of the spin-coating process.

476 Then, the films were annealed at 120 °C for 30 min to form the perovskite layer. For 2D perovskite

477 passivation at the top side, at the first step, PbI_2 beads were thermally evaporated (10^{-6} Torr) at an

478 evaporation rate of 0.5 Å s^{-1} to get thickness around 7, 15, and 25 nm. The second step is dropping

479 HBzA salt solution or mixture HBzA salt: FAI solution with 1:1 molar ratio (in mixture IPA and

480 DMF, 98:2 vol%) and then spin-coated at 2000 rpm for 30 s, followed by thermal annealing at

481 100 °C for 10 min. After this process, the perovskite films were stored overnight in vacuum

482 condition. All the process is done under N_2-glovebox with O_2 level was <10 ppm and H_2O level

483 was <0.1 ppm. Then the samples were transferred into a thermal evaporator for the C_{60} (25 nm)

484 and BCP (3 nm) deposition. For the final step, a 120 nm thick Ag layer was evaporated at low

485 pressure ($<10^{-6}$ Torr) with an area of ~0.1 cm^2. A ~120 nm MgF$_2$ was also evaporated at the glass

486 side to minimize the reflection losses from the glass substrates.

487 **Device Analysis**

488 The *J–V* curves were recorded using a Keithley 2400 source unit under AM 1.5 G (100 mW cm^{-2})

489 illumination with an Abet Technologies Sun 3000 solar simulator. The spectral mismatch was

490 calibrated using a KG-5 filter-covered mono-silicon standard cell (Newport). All devices were

491 measured in nitrogen filled glovebox for a sweep mode of reverse and forward scans with a

492 scanning rate of 0.1 V s^{-1}. The stabilized output of the devices was acquired by recording the power

493 output of the illuminated device at a constant voltage near the MPP extracted from the *J–V* curve.

494 External quantum efficiency spectra were obtained by passing the output of a 400 W Xenon lamp

495 through a monochromator and filter. Calibration was performed with a 603621 Calibrated Silicon

496 and Germanium Reference Detector. Activation energy measurement of ion migration. Electrical

497 poling was performed by applying different biases to the devices for 1 min in the dark; current-

498 voltage were measured with a Keithley 2401 source. Temperature dependence was measured with

499 a CTI cryogenic probe station with an attached Lakeshore 331 temperature controller under

500 vacuum (1×10^{-4} Pa). The temperature was monitored using a thermocouple placed in contact with

501 the sample. During the measurement, devices were first cooled to 10 K for 10 min and then heated

502 to adjust the temperature. The temperature was stabilized for 5 min prior to recording the current

503 for each step. Cross-section KPFM measurements were carried out using a home-built system

504 based on Bruker Dimension Icon atomic force microscope. The sample preparation and

505 measurements were conducted inside an Ar-filled glovebox. We used a Pt-Ir coated silicon probe

506 (PPP-EFM) and operate in tapping mode. The mapping was performed with 1024 pixels in the

507 fast-scan axis and more than 32 lines in the slow-scan axis, at a scan rate of 0.35 Hz. To ensure a

508 flat surface and expose all layers of the device, the cell was directly cleaved without polishing or

509 ion-milling. We then mapped the surface potential at the same location under dark and LED

510 illumination, with the LED providing white light of approximately 1 Sun intensity. To reduce the

511 noise level, we averaged the electrical potential profiles from all slow-scan lines. Next, we

512 subtracted the dark potential from the illuminated condition and calculated the first derivative to

513 obtain the electric field distribution across the device.

Sample Characterization

Field-emission SEM images were obtained with a JSM-7610F device (JEOL Ltd.). The PL emission was spectrally resolved using collection optic. For STEM based study, cross-sectional electron-transparent lamella was prepared in focused ion beam (FIB) equipped SEM-FIB Helios G4 DualBeam, FEI with help of an EasyLift nanomanipulator and Ga ion source. First protect the region of interest during FIB, two types of protective coatings were deposited: a 0.5 µm layer of Pt coating deposited by the e-beam, followed by a 3 µm layer of Pt coating deposited by the ion beam for final protection. Step by step ion beam milling procedure with beam current (2.4, 0.44, 0.26, 0.045, 0.025 nA for 30 to 5 kV) was carried out by cutting and thinning down lamella to 60 nm, while decreasing beam current (till 0.025 nA at 2 kV) to avoid ion beam damage. Additionally, low current cleaning process (5-2 kV, 81-28 pA) was performed to remove any potential contamination. STEM based experiments such as HAADF-STEM were performed in Cs Prob-corrected ThermoFisher Titan 60-300 Cubed TEM microscope operating at 300 kV.TEM data processing was performed using Gatan™ Digital Micrograph and Thermo Scientific™ Velox suites. For TEM and PL characterizations, the perovskite film samples preparation used 1:2 molar ratio of SAM and 2D ligand to help observation of 2D perovskites.

GIWAXS was conducted in the PLS-II 6D UNIST-PAL beamline of the Pohang Accelerator Laboratory (PAL), Korea. The energy of X-rays from the bending magnet was monochromatized to 18.986 keV (0.6530 Å) using a double-crystal monochromator. The 2D charge-coupled device detector (MX225-HS, Rayonix, LLC, USA) was used to record the 2D GIWAXS pattern, and the GIWAXS sample chamber was equipped with a 5-axis motorized stage for fine sample alignment. The sample-to-detector distance was 242.58 mm, and the diffraction angles were calibrated using NIST SRM660b, lanthanum hexaboride (LaB6). Incidence angle of ~0.2° was used for the GIWAXS measurements to obtain crystallographic information on the perovskite films used in this work.

XPS/UPS measurements were performed in a UHV chamber (ScientaOmicron) operating at a pressure of 5×10^{-10} mbar. UPS measurements were carried out using a 21.2 eV vacuum UV source (focus). The sample was biased by 10 eV to observe the low kinetic energy cutoff. The photoelectrons were collected at an angle of 80° between the sample and analyzer, with a normal electron take off angle. The constant analyzer pass energy was 5 eV for the valence band region

544 and for the secondary electron cut-off. XPS was carried out in the same spectrometer, equipped

545 with a monochromatic Al Ka X-ray Omicron XM1000 X-ray source (hv = 1486.6 eV) operating

546 at a power of 390 W. The high-resolution spectra were collected at a CAE of 15 eV. The spectra

547 were analyzed with Casa XPS software. The individual peak envelopes were fitted by a Gaussian

548 –Lorentzian (GL30) using a Tougaard based background function. Fourier-transform infrared

549 spectroscopy (FTIR) was conducted using Cary 600 Series FTIR Spectrometer (Agilent Tech.)

550 equipped with PIKE GladiATR geometry using diamond crystal in transmission mode. Samples

551 of powder were first dissolved into ethanol solvent and dried in a vacuum, then annealed at 100 °C

552 under N_2-glovebox for 10 min to completely remove the solvent. The dried powder samples are

553 spread uniformly above the crystal surface of FTIR. The spectral resolution was set to 4 cm^{-1} and

554 obtained by averaging 20 scans of each measurement. Transient PL decay and PLQY were

555 recorded using a spectrofluorometer (Fluoroma-Modular, Horiba Scientific). The 520 nm

556 calibrated pulse laser was generated from a picosecond laser diode (PicoQuant) equipped band-

557 pass 650 nm filter to collect 795 nm emitted light. The fluence is estimated to be around ~10

558 nJ/cm^2. For PLQY, an integrating sphere (Fluorolog, Horiba JobinYvon) was used and compared

559 with different tools using a JASCO FP-8500 spectrofluorometer equipped with an ILF-835

560 integrating sphere with the same procedure. It is noted that the results were consistent from two

561 different setups and measurements, confirming our reliability results as given in the statistical

562 PLQY values with a small deviation standard in Extended Data Fig. 6a.

563 **Device stability testing**

564 For the stability test, ~10 nm layer of tin (IV) oxide and an 80 nm layer of indium zinc oxide were

565 deposited on top of the C_{60} sequentially, by atomic layer and sputtering depositions, respectively,

566 to replace the BCP layer. The operational stability tests were carried out at the MPPT for the

567 encapsulated devices under 1 sun in ambient air (RH >50 %) at ~40 °C. The voltage at the MPPT

568 was automatically applied, and the power output of the devices was tracked. For the open-circuit

569 light soaking test, the devices were kept under full 1 sun illumination and constant temperature at

570 85 °C on hotplate in ambient air (RH above 50 %). The devices then measured periodically until

571 1000 h. The devices were encapsulated with simple glass and epoxy method. All processes were

572 done in N_2 glovebox.

573

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Author contributions

R.A. conceived, directed the research, and wrote the original draft. R.A., D.S.U., I.F.I, and A.P. fabricated the solar cells. B.V. conducted FIB and TEM measurements and analyses. A.M.R. performed the GIWAXS measurement and analysis. R.A. and A.M.R. performed PLQY measurement and analysis. S.Z. contributed to conceptualizing the idea of 2D perovskite and discussion at the bottom contact. P.D. performed XPS, IPES, and UPS measurements and did data analysis. R.A., D.S.U., and E.U. performed optical spectroscopy measurements and data analysis. D.S.U. performed SEM measurements. A.P. performed the top-surface KPFM measurement and did data analysis. R.A. performed and analysed the electronic characterization of the devices. F.C. performed cross-section KPFM and analysis. D.U. and A.A.S. performed the FTIR and analysis. I.F.I. helped to synthesized and characterized 2D perovskite layers. I.F.I. and A.A.S. performed the XRD measurement analysis. A.R.P. fabricated the aperture mask and determined the area. A.A.S. and A.S.S. helped to review the manuscript. E.A. contributed to reviewing and writing the manuscript. S.I.S. and C.X. supervised the project. S.D.W. supervised the overall project and secure the funding. All authors contributed to the manuscript.

Conflicts of Interest

The authors declare no competing interests.

Data availability

The data sets generated during and/or analysed during the current study are available from the corresponding author upon request.

603 **Extended Data Figure legends**

604 **Extended Data Fig. 1: Chemical analysis of SAMs and HBzA ligand. a**, Photograph of the
605 mixture 2PACz:HBzA (1:1 molar ratio) compound after drying under vacuum for a few days and
606 then annealed at 100 °C in a nitrogen glovebox to completely remove the solvent. The yellow
607 precipitated powder indicates the protonation between the first P–OH of the phosphonic group of
608 2PACz and the amine of HBzA molecules, forming an ionic bond. **b**, FTIR peaks of HBzA,
609 2PACz, and mixture (2PACz:HBzA, 1:1 molar ratio) in solid-state powder. The shifting peaks of
610 P–OH at ~950 cm^{-1} and ~1033 cm^{-1} to the higher wavenumber of the mixture compound indicate
611 stronger bonding due to deprotonation of the first P–OH group of the phosphonic acid of 2PACz.
612 Consequently, the additional new peak associated with the P–O bond at 1105 cm^{-1} is formed. In
613 contrast, N–H bending peaks of the amine group (HBzA) at ~1530 cm^{-1} and 1620 cm^{-1} are shifted
614 to the lower wavenumber with enhanced intensity in the mixture compound, presumably due to
615 the protonation of –NH$_2$ to –NH$_3^+$. These results successfully confirm the acid-base reaction
616 between the pK_{a1} of the phosphonic acid and the pK_b of alkyl amines, as illustrated in **Fig. 1a**. **c**,
617 XPS analysis of 2PACz on ITO film. High-resolution spectra of C1s of 2PACz, HBzA, and a
618 mixture of 2PACz+HBzA onto ITO after washing with DMF/DMSO.

619 **Extended Data Fig. 2: SKPM mapping images and distributions of WF. a**, ITO/2PACz+HBzA
620 sample before and after washing. The DMF/DMSO solvent mixture was used to wash the
621 ITO/2PACz+HBzA sample. The minor WF shifting of the ITO/2PACz+HBzA sample before and
622 after washing with DMF/DMSO indicates a strong attachment of HBzA molecules onto 2PACz
623 molecules, consistent with XPS results. **b**, ITO/2PACz sample after washing. **c**, Bare ITO. **d**,
624 SKPM mapping images of ITO/2PACz/perovskite and ITO/2PACz+HBzA/perovskite samples
625 after washing with DMF/DMSO. **e**, Distributions of WF of both samples from KPFM
626 measurement. After the perovskite film deposition and subsequent removal of the HBzA ligands,
627 the WF of ITO/2PACz+HBzA is shifted back to the WF of pristine ITO/2PACz (~5.40 eV),
628 confirming our hypothesis.

629 **Extended Data Fig. 3: Statistics of PCE, V_{OC}, and FF of PSCs. a**, Bottom-side 2D/3D with
630 different molar ratios of 2PACz: HBzA. **b**, Bottom-side 2D/3D with various 2D ligands
631 (benzylamine, BzA; phenethylamine, PEA; butylamine, BA; hexylmethylamine, HMA) for
632 bottom-side 2D/3D heterojunction with a 1:1 molar ratio of 2PACz. **c**, Top-side 3D/2D with PbI$_2$
633 thickness variation for top-side 3D/2D heterojunction. The statistics are obtained from 10 to 20
634 cells for each condition from different batches. It is noted that the perovskite used here is based on
635 Cs$_{0.05}$FA$_{0.95}$PbI$_3$.

636 **Extended Data Fig. 4: Energetic alignment analysis. a**, Energy level scheme for 2PACz
637 anchored on ITO, 3D-perovskites, 2D-perovskites on top and bottom interfaces, and C$_{60}$ layers
638 extracted from UPS data. The VBM was obtained as hv – (E$_{cutoff}$ – E$_{VB, min}$). The position of the
639 CBM with respect to the VBM was defined by extracting E_g (~1.53 eV) from EQE in
640 Supplementary Fig. 8 for 3D-perovskite and by IPES for 2D-perovskite with $n = 2$ ($E_g = $ ~2.1 eV).
641 **b**, **c**, Secondary electron cut-off and valence spectra plots from UPS measurement. **d**, IPES spectra
642 of the 2D perovskite film with $n = 2$ using the hybrid method.

643 **Extended Data Fig. 5: Device performance with double-cation perovskite. a**, Representative
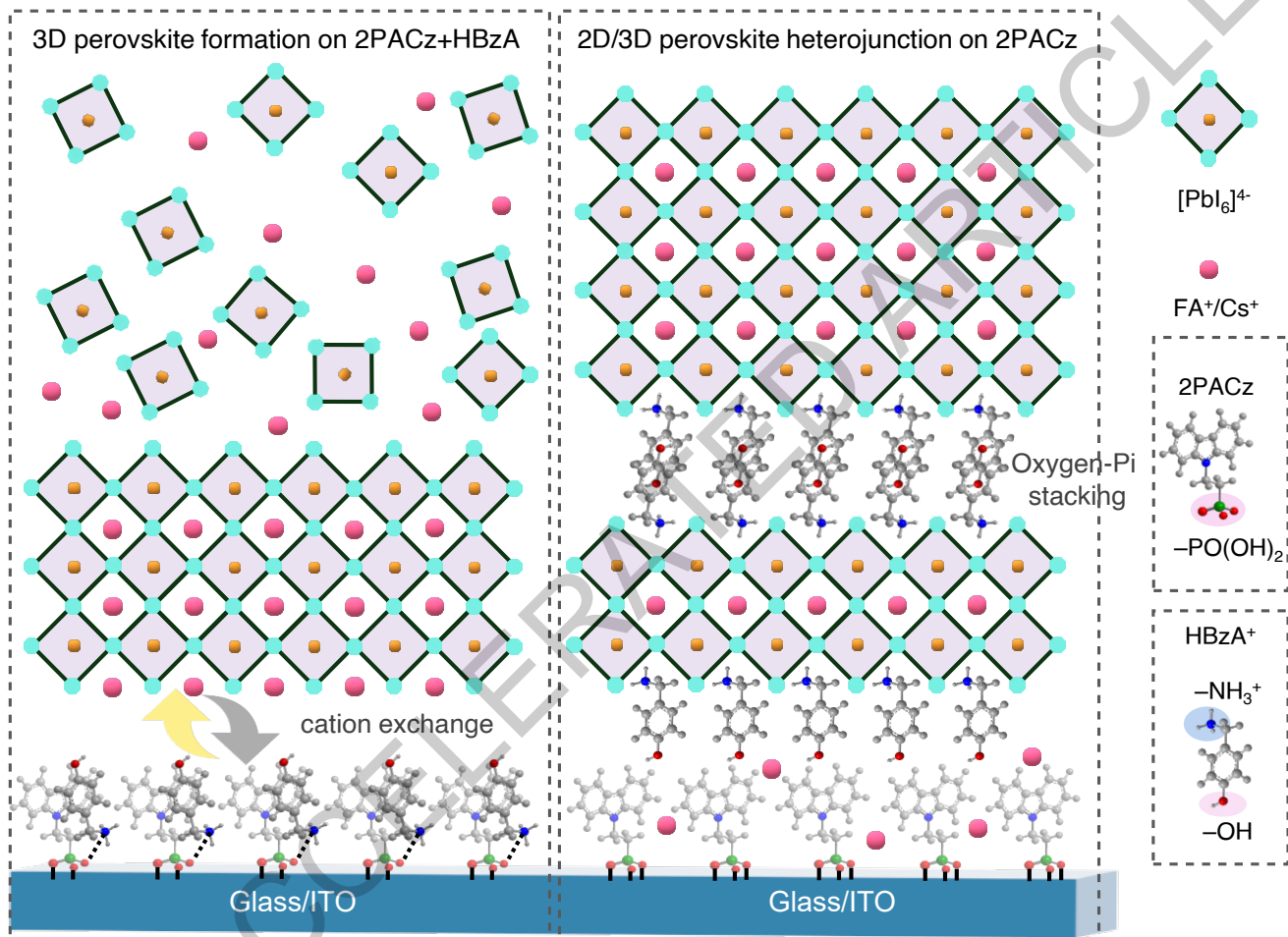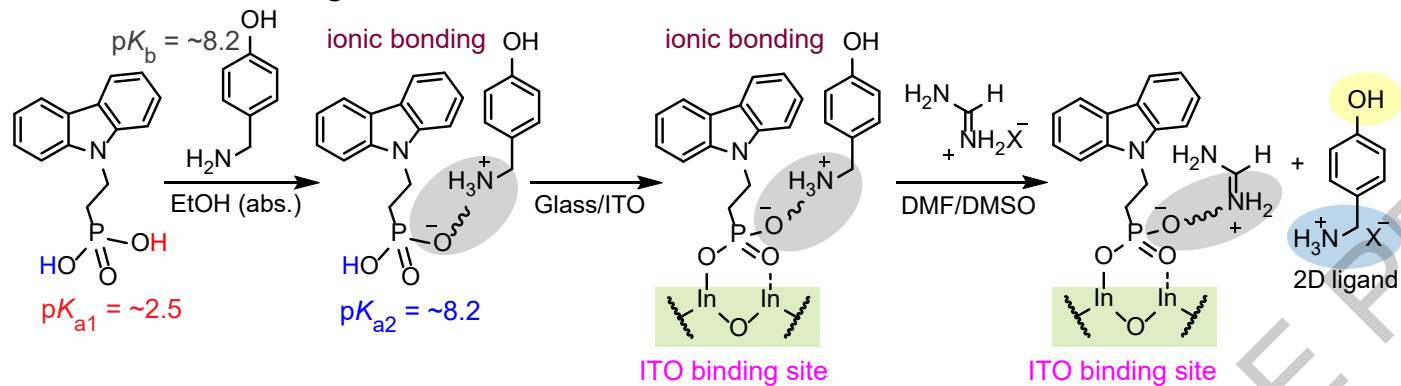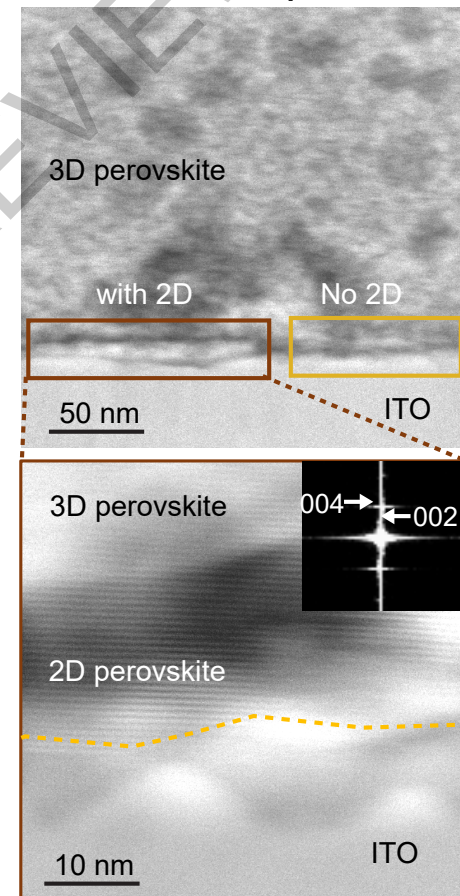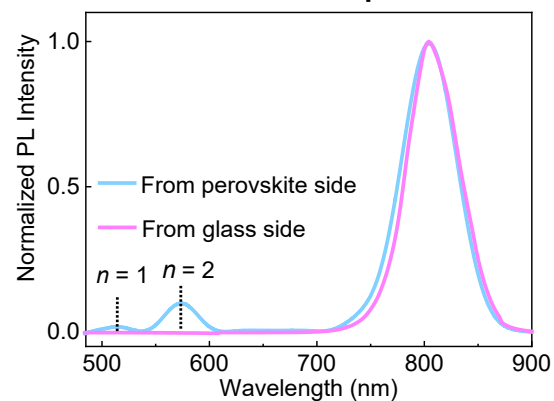644 $J–V$ curve for control and double-side 2D/3D heterojunctions perovskite solar cells with

645 $Cs_{0.05}FA_{0.95}PbI_3$ perovskite, achieving a maximum PCE of 25.2% under reverse scan. Statistical
646 parameters of (**b**) PCE, (**c**) V_{OC}, and (**d**) FF values of PSCs. The statistical parameters are obtained
647 from 50 cells for each condition from different batches.
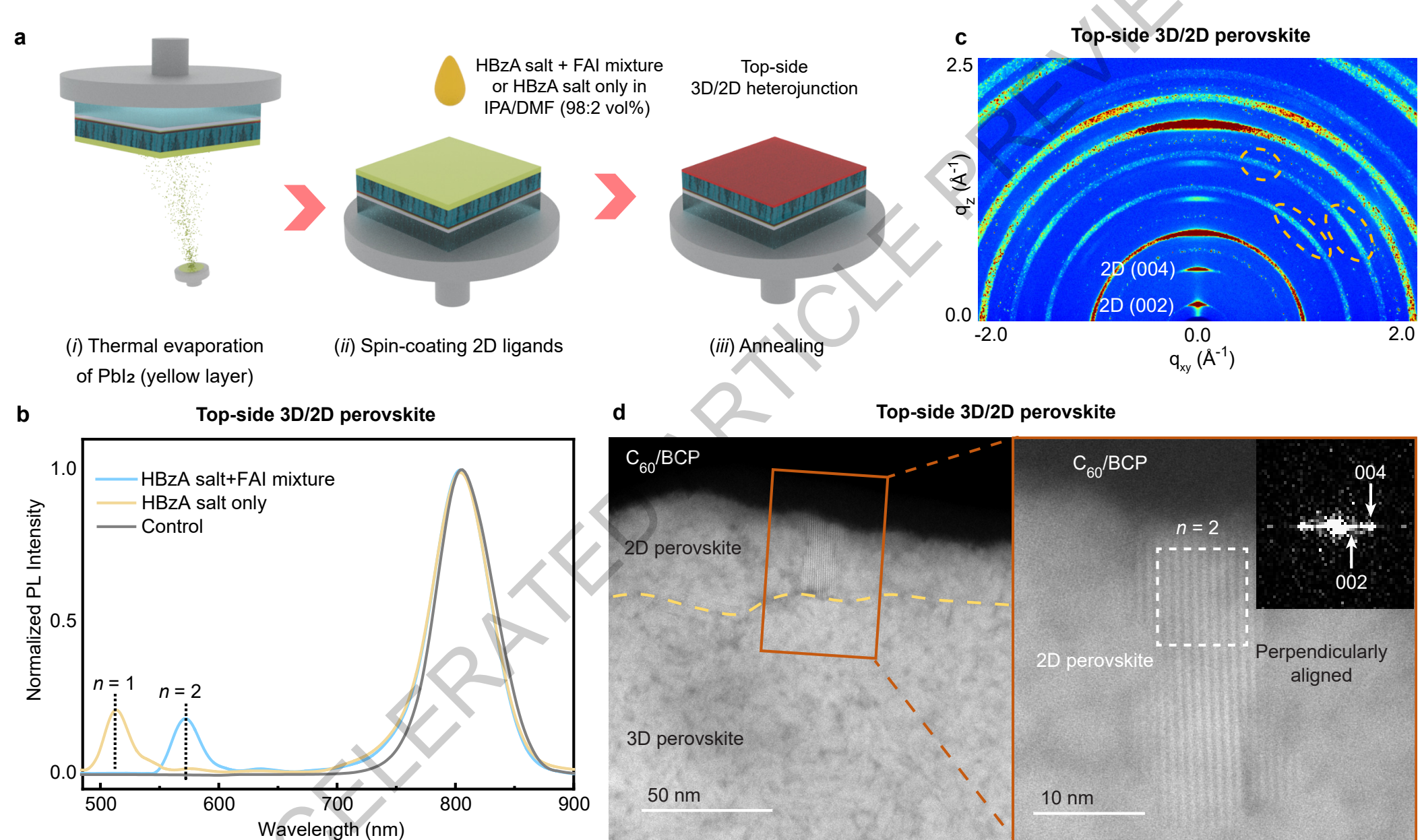
648 **Extended Data Fig. 6: Passivation and trap analysis. a**, PLQY results, and (**b**) transient PL
649 decays of perovskite films on various 2D/3D heterojunctions. **c**, **d**, SCLC plots for control and
650 double-side 2D/3D heterojunction-based devices of (**c**) electron-only and (**d**) hole-only devices. **e**,
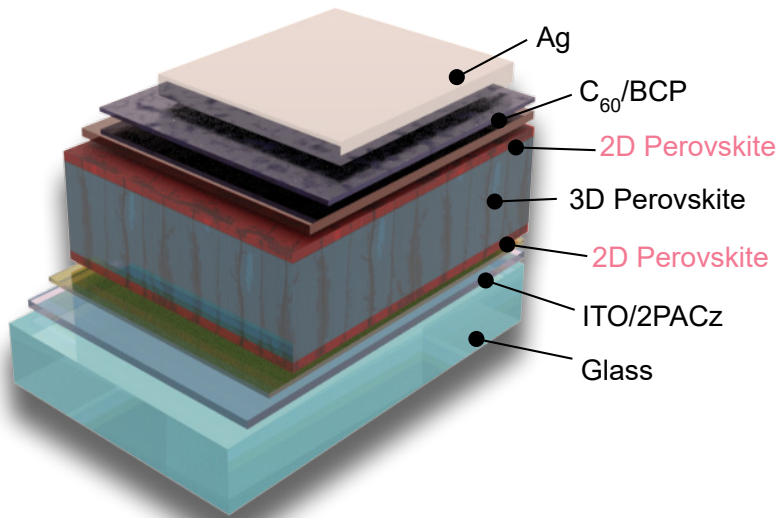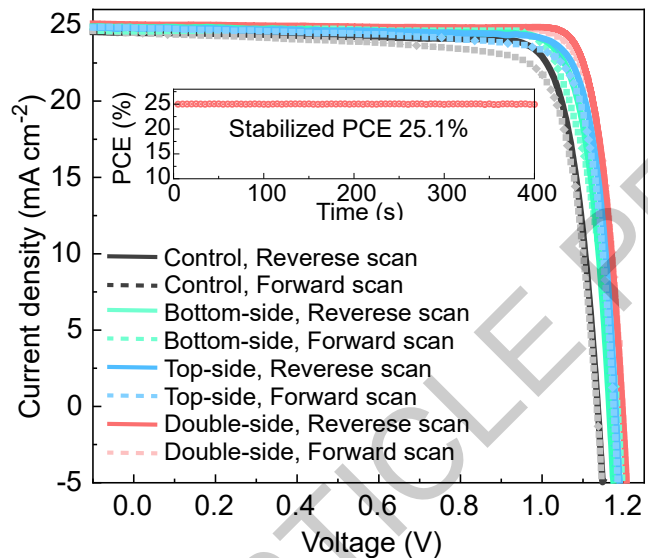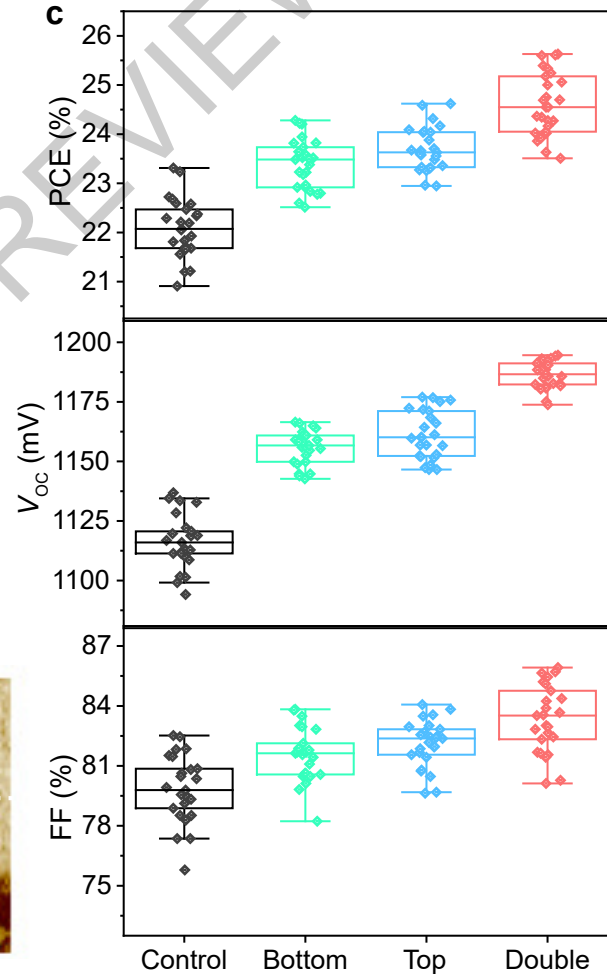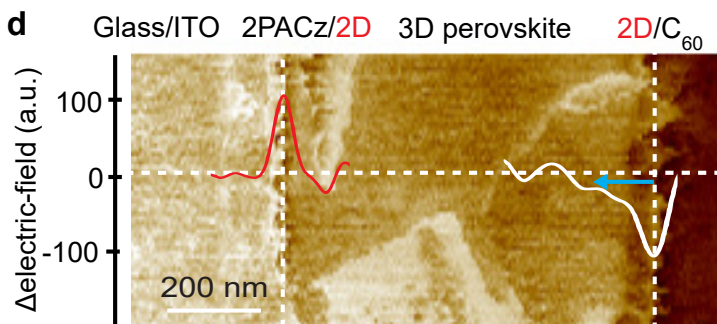651 TAS analysis of control, bottom-side, and double-side 2D/3D passivation-based devices.

652 **Extended Data Fig. 7: Stability and ion migration analysis. a**, **b**, UV-vis absorbance spectra
653 evolution of iodine in toluene solution for the control (**a**) and double-side passivation of perovskite
654 films (**b**) at different aging times. Inset is a photo of the sealed vials with the control and 2D/3D
655 perovskite films, taken after 100 h of light and heat exposures. **c**, Temperature-dependent
656 conductivity of control and double-side 2D/3D perovskite films.

657

a Mechanism of 2D ligand formation and release from the ITO/2PACz surface

$pK_b = {\sim}8.2$

ionic bonding

ionic bonding

$pK_{a1} = {\sim}2.5$

$pK_{a2} = {\sim}8.2$

Glass/ITO

DMF/DMSO

ITO binding site

ITO binding site

2D ligand

3D perovskite formation on 2PACz+HBzA

2D/3D perovskite heterojunction on 2PACz

Oxygen-Pi stacking

cation exchange

Glass/ITO

Glass/ITO

$[PbI_6]^{4-}$

FA^+/Cs^+

2PACz

$-PO(OH)_2$

HBzA$^+$

$-NH_3^+$

$-OH$

b Bottom-side 2D/3D perovskite

3D perovskite

with 2D

No 2D

50 nm

ITO

3D perovskite

004→   ←002

2D perovskite

10 nm

ITO

c Bottom-side 2D/3D perovskite

Normalized PL Intensity

From perovskite side

From glass side

$n = 1$ $n = 2$

Wavelength (nm)

a

(*i*) Thermal evaporation of PbI₂ (yellow layer)

HBzA salt + FAI mixture or HBzA salt only in IPA/DMF (98:2 vol%)

(*ii*) Spin-coating 2D ligands

Top-side 3D/2D heterojunction

(*iii*) Annealing

b

Top-side 3D/2D perovskite

- HBzA salt+FAI mixture
- HBzA salt only
- Control

n = 1

n = 2

Normalized PL Intensity

Wavelength (nm)

c

Top-side 3D/2D perovskite

q_z (Å^{-1})

q_{xy} (Å^{-1})

2D (004)

2D (002)

d

Top-side 3D/2D perovskite

C₆₀/BCP

2D perovskite

3D perovskite

50 nm

C₆₀/BCP

n = 2

2D perovskite

Perpendicularly aligned

004

002

10 nm

a

Ag
C$_{60}$/BCP
2D Perovskite
3D Perovskite
2D Perovskite
ITO/2PACz
Glass

b

Current density (mA cm^{-2})

Voltage (V)

PCE (%) · Time (s) · Stabilized PCE 25.1%

Control, Reverese scan
Control, Forward scan
Bottom-side, Reverese scan
Bottom-side, Forward scan
Top-side, Reverese scan
Top-side, Forward scan
Double-side, Reverese scan
Double-side, Forward scan

c

PCE (%)
V_{OC} (mV)
FF (%)

Control   Bottom   Top   Double

d

Glass/ITO   2PACz/2D   3D perovskite   2D/C$_{60}$

Δelectric-field (a.u.)

200 nm

e

Glass/ITO   2PACz   3D perovskite   C$_{60}$

Δelectric-field (a.u.)

200 nm

f

PCE (%)

Time (h)

Control 3D
Bottom-side
Top-side
Double-side

Light +Thermal
ITO/2PACz/CsFAPbI$_3$/C$_{60}$/SnO$_2$/IZO/Cu

g

PCE (%)

Time (h)

T$_{90}$

MPPT
ITO/2PACz/2D/3D-CsFAPbI$_3$/2D/C$_{60}$/SnO$_2$/IZO/Cu

Double-side

a

b

c

Extended Data Fig. 1

ITO/2PACz+HBzA

ITO/2PACz+HBzA (washing)

50.0 mV

−50.0 mV

0.0　Potential　2.0 µm

ITO/2PACz

50.0 mV

−50.0 mV

0.0　Potential　2.0 µm

ITO

ITO/2PACz/3D-perovskite (washing)

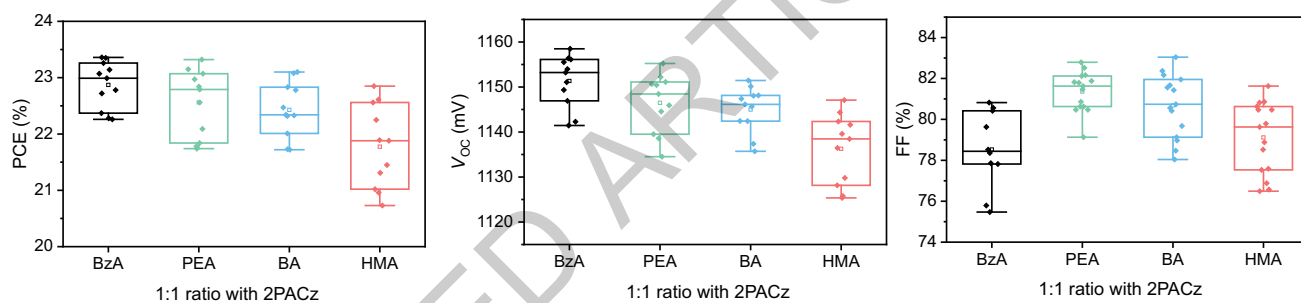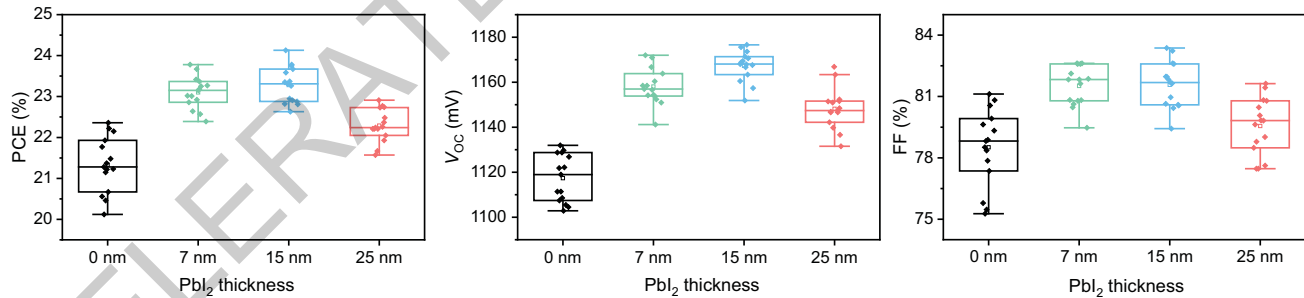ITO/2PACz/2D-HBzA/3D-perovskite (washing)

50.0 mV

−50.0 mV
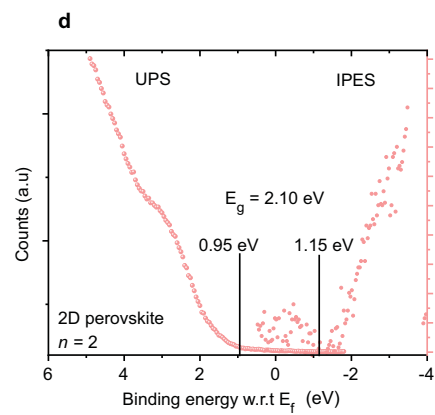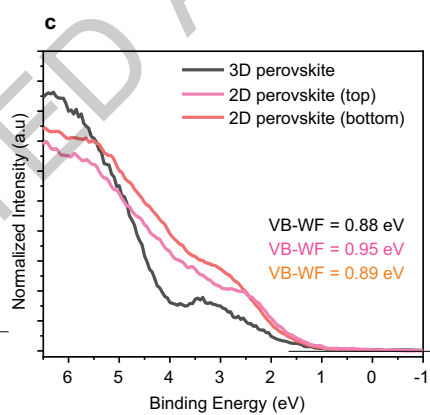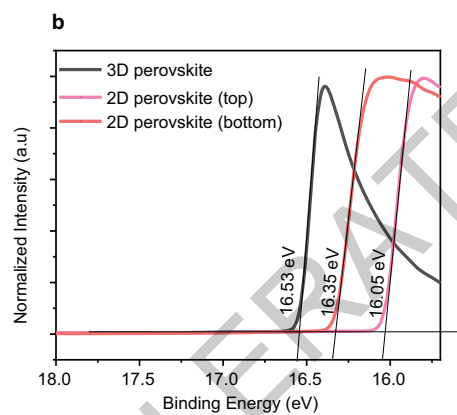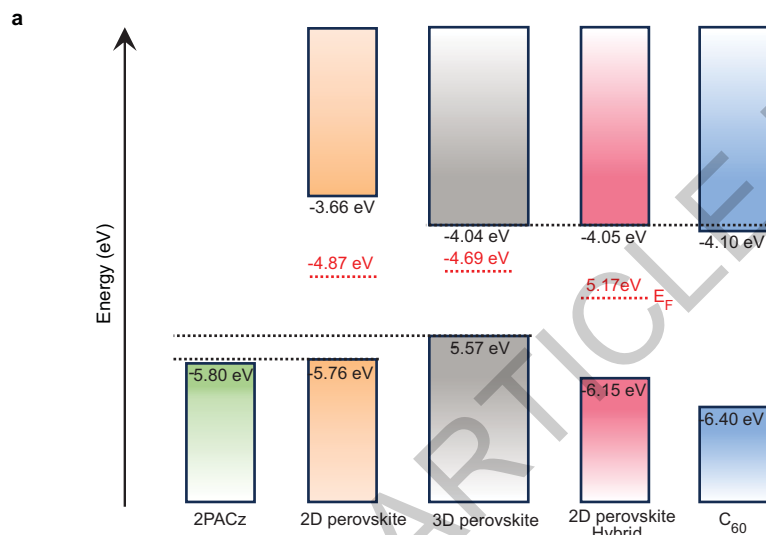
0.0　Potential　2.0 µm

Extended Data Fig. 2
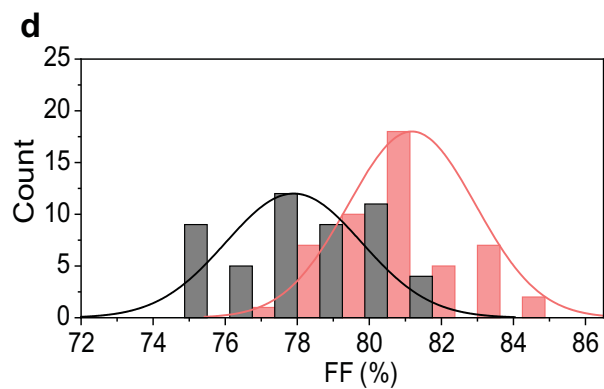
a   Bottom-side 2D/3D heterojunction

b   2D/3D at bottom with various ligands

c   Top-side 3D/2D heterojunction

Extended Data Fig. 3

a

2PACz: -5.80 eV, -4.87 eV

2D perovskite: -3.66 eV, -5.76 eV

3D perovskite: -4.04 eV, -4.69 eV, 5.57 eV

2D perovskite Hybrid: -4.05 eV, 5.17eV E_F, -6.15 eV

C_{60}: -4.10 eV, -6.40 eV

Energy (eV)

b

- 3D perovskite
- 2D perovskite (top)
- 2D perovskite (bottom)

Normalized Intensity (a.u)

16.53 eV, 16.35 eV, 16.05 eV

Binding Energy (eV)

c

- 3D perovskite
- 2D perovskite (top)
- 2D perovskite (bottom)

Normalized Intensity (a.u)

VB-WF = 0.88 eV
VB-WF = 0.95 eV
VB-WF = 0.89 eV

Binding Energy (eV)

d

UPS   IPES

Counts (a.u)

E_g = 2.10 eV

0.95 eV   1.15 eV

2D perovskite
n = 2

Binding energy w.r.t E_f (eV)

Extended Data Fig. 4

Extended Data Fig. 5

a

PLQY (%)

Control 3D, 2D/3D, 3D/2D, 2D/3D/2D, Control 3D/C$_{60}$, 2D/3D/2D/C$_{60}$

b

PL intensity (a.u.)

Time (μs)

2D/3D/2D (τ_{ave} = 2.69 μs)
2D/3D (τ_{ave} = 1.34 μs)
3D/2D (τ_{ave} = 1.73 μs)
Control 3D (τave = 0.97 μs)
Fitting

c

Current density (mA cm^{-2})

Applied Voltage (V)

Control
Double-side 2D/3D

SCLC region

V_{TFL} = 0.71 V

V_{TFL} = 1.80 V

Ohmic region

Trap-filling limited region

Electron-only device

d

Current density (mA cm^{-2})

Applied Voltage (V)

Control
Double-side 2D/3D

SCLC region

V_{TFL} = 0.75 V

V_{TFL} = 1.78 V

Ohmic region

Trap-filling limited region

Hole-only device

e

tDOS (cm^3 eV^{-1})

E_{ω}(eV)

Control 3D
Bottom-side 2D/3D
Double-side 2D/3D

Extended Data Fig. 6

a

Control 3D perovskite

100 hrs
50 hrs
20 hrs
0 hrs

Absorbance (a.u.)

Wavelength (nm)

b

Double-side 2D/3D

100 hrs
50 hrs
20 hrs
0 hrs

Absorbance (a.u.)

Wavelength (nm)

c

$E_a = 0.27$ eV

$E_a = 0.47$ eV

Control
Double-side

$\ln(\sigma T)$

$1/kT$ (eV)

Extended Data Fig. 7