

1 **Bright and stable perovskite light-emitting diodes in the near-infrared**
2 **range**

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27

28 **Abstract**

29

30 Perovskite light-emitting diodes (LEDs) have attracted broad attention due to their rapidly
31 increasing external quantum efficiencies (EQEs)¹⁻¹⁵. However, most high EQEs of perovskite
32 LEDs are reported at low current densities ($< 1 \text{ mA cm}^{-2}$) and low brightness. Decrease in
33 efficiency and rapid degradation at high brightness inhibit their practical applications. Here,
34 we demonstrate perovskite LEDs with exceptional performance at high brightness, achieved
35 by the introduction of a multifunctional molecule that simultaneously removes non-radiative
36 regions in the perovskite films and suppresses luminescence quenching of perovskites at the
37 interface with charge-transport layers. The resulting LEDs emit near-infrared light at 800
38 nanometres, exhibit a peak EQE of 23.8 % at 33 mA cm^{-2} and retain EQEs over 10 % at high
39 current densities of up to $1,000 \text{ mA cm}^{-2}$. In pulsed operation, they retain EQE of 16 % at an
40 ultra-high current density of $4,000 \text{ mA cm}^{-2}$, along with a high radiance of over $3,200 \text{ W s}^{-1} \text{ m}^{-2}$.
41 Notably, an operational half-lifetime of 32 hours at an initial radiance of $107 \text{ W s}^{-1} \text{ m}^{-2}$ has been
42 achieved, representing the best stability for perovskite LEDs having EQEs exceeding 20% at
43 high brightness levels. The demonstration of efficient and stable perovskite LEDs at high
44 brightness is an important step toward commercialisation and opens up new opportunities
45 beyond conventional LED technologies, such as perovskite electrically pumped lasers.

46

47 **Main**

48

49 Solution-processable metal halide perovskites exhibit luminescence with high colour purity,
50 tuneable emission wavelengths and excellent charge-transport properties. They have been
51 considered as potential candidates for high-performance light-emitting diodes (LEDs)¹⁻¹⁵ with
52 low cost, flexibility and light weight. In the past decade, perovskite LEDs have been
53 extensively optimised, often by incorporation of molecular additives⁵⁻⁹, and external quantum
54 efficiencies (EQEs) of over 20 % have been achieved⁵⁻⁹. The emergence of more efficient
55 perovskite LEDs continues, along with improved stability at low brightness. However, high
56 EQEs and improved stability were mostly reported at low current densities and brightness.
57 Retaining EQE and stability at high brightness is already the key challenge for
58 commercialisation of perovskite LEDs.

59

60 In this work, we design a multifunctional molecule 2-[4-(methylsulfonyl)phenyl]ethylamine
61 (MSPE, **Fig. 1a**) to manipulate the optoelectronic, crystal and morphological properties of 3D
62 cubic phase (α -phase) formamidinium (FA) lead triiodide (FAPbI₃) perovskites and
63 demonstrate efficient and operationally stable near-infrared (NIR) perovskite LEDs at high
64 brightness. MSPE improves crystallinity and photoluminescence efficiency and induces
65 homogenous emission by removing non-radiative dark regions in the perovskite films. As a
66 multifunctional additive, MSPE also provides a barrier to quenching of perovskite
67 luminescence at the interface with charge-transport layers. In addition, MSPE devices show
68 reduced Joule heating, which allows high EQE to be maintained at ultra-high current densities
69 and reduces thermal degradation.

70

71 We fabricated FAPbI₃-based perovskite LEDs with the device architecture as follows: glass/
72 indium tin oxide (ITO, 150 nm)/ zinc oxide (ZnO, 35 nm)/ ethoxylated polyethylenimine (PEIE,
73 ~ 0.5 nm)/ perovskite (FAPbI₃, 30 nm)/ poly(4-butylphenyl-diphenylamine) (poly-TPD,
74 40 nm)/ molybdenum oxide (MoO_x, 7 nm)/ gold (Au, 60 nm) (**Fig. 1b**). ITO and Au function
75 as electrodes. ZnO and poly-TPD serve as electron- and hole-transport layers, respectively. A
76 thin PEIE layer is used to improve the wettability of ZnO. MoO_x acts as the hole-injection layer.
77 The FAPbI₃ perovskites were prepared via spin-coating from FAI, PbI₂ and MSPE precursors
78 at a molar ratio of 2.7: 1: x ($x = 0 - 0.9$). The device performance is dependent on the molar
79 fraction of MSPE relative to PbI₂ (**Fig. 1d**, Supplementary Fig. 1). As a 0.5 molar fraction of

80 MSPE/PbI₂ exhibits the best device performance, the films and devices with this composition
81 are hereafter referred to as “MSPE”. The samples without MSPE are referred to as “control”.
82 The angle-dependent electroluminescence (EL) intensity of MSPE-based LEDs follows a
83 Lambertian profile (**Fig. 1c**). The current density–voltage–radiance (J – V – R) characteristic of a
84 champion MSPE LED is shown in **Fig. 1e**. The current density and radiance of MSPE LEDs
85 rise rapidly after 1.3 V, which is lower than the bandgap voltage of FAPbI₃ (1.55 eV) and
86 indicates efficient charge transport and injection^{16,17}. Their EL peaks at 800 nm with a narrow
87 full-width at half-maximum of 39 nm and has a stable shape under bias (**Fig. 1f**). The champion
88 MSPE-based devices have a peak EQE of 23.8 % at a high radiance of 39 W sr⁻¹ m⁻² (**Fig. 1e**,
89 **f**). The brightness rises quickly with voltage and yields 497 W sr⁻¹ m⁻² (photon flux of $6.3 \times$
90 10^{21} m⁻² s⁻¹) at 4.4 V. It is noteworthy that an EQE of over 10 % is retained at high current
91 densities of up to 1,000 mA cm⁻². The maximum radiance achieved is 663 W sr⁻¹ m⁻² in another
92 device with a peak EQE of 22.2 %. Note that radiance is used to evaluate brightness of NIR
93 LEDs, as luminance only applies to visible light (Supplementary Note 1)¹⁸. These NIR emitters
94 are attractive for a wide variety of applications such as imaging¹⁹, optogenetics²⁰, night-vision²¹,
95 communication²² and lasing^{23,24}. To the best of our knowledge, in the NIR regime, this
96 combination of high EQE and high radiance found in MSPE-based LEDs is superior to
97 previously reported perovskite, organic, and quantum-dot LEDs (**Fig. 1g**).

98
99 MSPE devices exhibit high energy conversion efficiency (ECE) of up to 16 % (Supplementary
100 Fig. 2). This implies reduction of the electrical power and Joule heating to drive the devices,
101 allowing EQE to be maintained at high brightness and prolonging the device lifetime. MSPE-
102 based LEDs show a rapid increase in radiance and a smaller increase in device temperature
103 during the voltage scan compared to control ones (Supplementary Fig. 3). To relieve Joule
104 heating, pulsed voltages have been applied to devices, which enables sufficient time for heat
105 dissipation. As a result, MSPE devices achieve EQE of 16 % at an ultrahigh current density of
106 4,000 mA cm⁻², along with a high radiance of over 3,200 W sr⁻¹ m⁻².

107
108 Furthermore, MSPE-based LEDs show reasonable reproducibility. We fabricated 42 devices
109 with the same procedures and their peak EQE and radiance histograms are shown in **Fig. 1h**.
110 The histograms show a mean EQE of 20 % with a standard deviation of 1.6 % and a mean peak
111 radiance of nearly 500 W sr⁻¹ m⁻². MSPE LEDs with a simple glass-epoxy encapsulation
112 exhibit a half-lifetime (T_{50} , the time to reach 50 % of the initial brightness) of 32 hours for a
113 very high initial radiance of 107 W sr⁻¹ m⁻² at a constant current density of 100 mA cm⁻² (**Fig.**

114 **ii).** EL spectra and voltages were stable during lifetime measurement (Supplementary Fig. 4-
115 5). The control devices show poor T_{50} of 5 hours for an initial radiance of $\sim 10 \text{ W sr}^{-1} \text{ m}^{-2}$
116 (Supplementary Fig. 6). MSPE LEDs represent the best stability for perovskite LEDs having
117 EQE exceeding 20 % at high brightness levels (Supplementary Fig. 4; Supplementary Table.
118 1-2). To predict lifetimes at lower radiance, we fitted measured lifetimes at various initial
119 radiances with an empirical formula^{15,25}. For an initial radiance of $5 \text{ W sr}^{-1} \text{ m}^{-2}$, T_{50} of MSPE
120 devices is estimated to be 5×10^4 hours (Supplementary Fig. 4), comparable to the state-of-
121 the-art organic and quantum-dot LEDs (Supplementary Table. 3).

122

123 To understand the underlying reasons for the improved performance of MSPE-based devices,
124 we performed film characterisations as follows. Grazing-incidence wide-angle X-ray
125 scattering (GIWAXS) measurements show that both films exhibit typical α -phase scattering
126 characteristics at around 1 \AA^{-1} (**Fig. 2a**). The scattering characteristics of the control film are
127 isotropic, indicating that perovskite crystallites are randomly oriented²⁶. MSPE induces an
128 oriented crystallization as GIWAXS shows a preferential orientation of perovskites along the
129 surface normal direction^{27,28}. X-ray diffraction (XRD) analysis shows the sharp and strong
130 peaks of α -phase FAPbI₃ in the MSPE film, indicating vastly improved crystallinity
131 compared to the control film (**Fig. 2d**)²⁹. Hyperspectral microscopy further unveils the
132 heterogeneities of PL peak wavelength across the control films (**Fig. 2b**), indicating disorder
133 of local energetic structure. MSPE significantly mitigates this disorder, leading to uniform
134 peak wavelength in the films (**Fig. 2b**). Crystallographic and energetic disorder provides non-
135 radiative recombination centres undermining device performance^{26,30}, which are mitigated by
136 MSPE. Consequently, MSPE films show improved PLQEs over a wide range of excitation
137 intensity (**Fig. 2e**). Their PLQEs remain over 40 % even at a low excitation intensity of 0.02
138 mW cm^{-2} , indicating reduced defect-mediated non-radiative recombination in MSPE films.
139 Reduction of defect-mediated recombination is also confirmed by time-resolved PL
140 spectroscopy as MSPE shows slower PL decay (Supplementary Fig. 7).

141

142 Nanoscopic morphology and emission properties of these films are further investigated. From
143 scanning electron microscopy (SEM, **Fig. 2c**), irregular and discontinuous perovskite
144 polycrystalline grains are distributed on top of ZnO substrate in the control samples. Perovskite
145 grains in MSPE films are denser and adopt a regular island shape. Atomic force microscopy
146 (AFM, Supplementary Fig. 8) shows similar morphology to SEM. From AFM, the root mean

147 square surface roughness reduces from 13.7 nm to 3.6 nm with the addition of MSPE, which
148 could be attributed to a thin organic layer filling in the gaps between perovskite grains⁵. Then
149 cathodoluminescence (CL) signals from SEM visualise the emission profile of these grains
150 (**Fig. 2c**). MSPE films have mean CL intensity of 11.7 counts, more than twice stronger than
151 that of the control ones (4.8 counts) under the same acquisition conditions. Strong CL intensity
152 indicates that luminescence efficiency is promoted with MSPE (Supplementary Note 2). MSPE
153 also slows down the degradation of perovskites under electron beam exposure (Supplementary
154 Fig. 9). These observations confirm that MSPE reduces non-radiative recombination in the
155 perovskite grains, consistent with the PL measurements.

156

157 The improved quality of perovskite films is attributed to MSPE, the roles of which are further
158 unveiled by Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron
159 spectroscopy (XPS), nuclear magnetic resonance (NMR) and density functional theory (DFT)
160 simulations. FTIR reveals that the amino group scissoring vibration $\delta(\text{NH}_2)$ of MSPE at
161 around 1646 cm^{-1} is significantly broadened and nearly invisible in the MSPE + FAI sample
162 (**Fig. 2f**), indicating that the N-H chemical bond is greatly weakened by the addition of FAI.
163 Consistent with this, ^{127}I NMR spectrum of FAI is significantly broadened with the addition
164 of MSPE (**Fig. 2g**). Strong interaction with FAI could slow down the growth of perovskites
165 during film formation, contributing to high crystallinity and regular shape of grains
166 (Supplementary Note 3; Supplementary Fig. 16-18). The sulfonyl group can interact with FAI
167 or PbI_2 as the stretching vibration $\nu(\text{S}=\text{O})$ is broadened and shifts to lower wavenumbers in
168 both mixture samples (**Fig. 2f**). XPS further unveils that the Pb 4*f* signals of PbI_2 shift to
169 lower binding energies with MSPE (**Fig. 2h**), while the O 1*s* signal of MSPE shifts to higher
170 binding energy (Supplementary Fig. 10), indicating that the oxygen atoms in the sulfonyl
171 group can donate their lone electron pairs to the empty 6*p* orbital of Pb atoms⁸. This suggests
172 that unsaturated Pb dangling bonds due to halide vacancy can be passivated by MSPE. DFT
173 simulations reveal trap-free bandgap of perovskites with MSPE passivation and further show
174 that both amino group and sulfonyl group can bind with perovskites (Supplementary Fig. 11).

175

176 MSPE can also interact with other MSPE molecules through hydrogen bonding. FTIR
177 measurements of MSPE molecules with different concentrations were performed. Both
178 $\delta(\text{NH}_2)$ and $\nu(\text{S}=\text{O})$ signals are broadened as the concentration of MSPE increases (**Fig. 2i**),
179 suggesting hydrogen bonding interactions between the amino group and the sulfonyl group of

180 MSPE (N-H \cdots O=S). Hydrogen bonding between two functional groups is further examined
181 by using methyl phenyl sulfone (MPS, with a sulfonyl group) and phenethylamine (PEA,
182 with an amino group) (Supplementary Fig. 12). The addition of MPS causes upfield-shifting
183 of ^1H NMR signals of the amino group in PEA, indicating increasing electron density due to
184 hydrogen bonding (N-H \cdots O=S). Consistent with this, FTIR also suggests that both the
185 sulfonyl group of MPS and the amino group of PEA are broadened in the mixture sample
186 (Supplementary Fig. 12).

187

188 The above investigations reveal the roles of the multifunctional molecule MSPE. MSPE
189 induces high crystallinity and reduces various defects in perovskite films, leading to
190 improved PLQE and reduced crystallographic and energetic disorder (**Fig. 2a-e**). Charge-
191 carrier kinetics further confirm the reduction of defects and disorder in MSPE films (**Fig. 3**).
192 In addition, MSPE can assemble in between perovskite grains through hydrogen bonding and
193 form a physical spacer between charge-transport layers, removing interfacial quenching
194 pathways (**Fig. 4**).

195

196 Confocal PL microscopy shows that the control films have significant spatial variation in PL
197 intensity on the lengthscale of micrometres (**Fig. 3a**). The dark regions in the control samples
198 correlate with reduced PL lifetime, indicating that these dark regions contain a higher
199 concentration of defects serving as non-radiative centres^{31,32}. In contrast, the MSPE films show
200 much more homogenous intensity and a uniformly long lifetime on the same lengthscale (**Fig.**
201 **3c**). The absence of defect-containing dark regions in MSPE films is consistent with the
202 improved overall PLQE and carrier lifetime relative to the control films. Quantitative analysis
203 of the recombination process by transient absorption measurements was performed to evaluate
204 the defect concentration of perovskite films (Supplementary Fig. 13). The defect-mediated non-
205 radiative recombination (k_1), bimolecular recombination (k_2), and Auger recombination (k_3)
206 rate constants are extracted from the rate equation for charge carrier population (Supplementary
207 Note 4). As shown in **Fig. 3b** and **d**, k_1 of MSPE films ($6.2 \times 10^6 \text{ s}^{-1}$) is nearly an order of
208 magnitude lower than that of the control films ($4.2 \times 10^7 \text{ s}^{-1}$), indicating a significant decrease
209 of defect density with the introduction of MSPE molecules. Photothermal deflection
210 spectroscopy (PDS) also reveals reduced defect concentrations in MSPE films (Supplementary
211 Fig. 14)³³.

212 Another function of the MSPE additive is to prevent luminescence quenching of perovskites at
213 the charge-transport interfaces. In the control devices, since perovskite grains are discontinuous
214 on ZnO (**Fig. 2c**, Supplementary Fig. 1), poly-TPD on top of perovskites can directly contact
215 with ZnO as demonstrated in **Fig. 4a**. PDS shows that the ZnO + poly-TPD mixture sample
216 forms interfacial states with energies lower than the bandgap of FAPbI₃ (Supplementary Fig.
217 15), which can quench the emission of perovskites and serve as non-radiative loss channels
218 undermining device performance. To investigate interfacial quenching, the PL decay kinetics
219 of perovskites in multilayer systems were measured by selectively exciting the perovskites with
220 a 560 nm laser where charge-transport materials have negligible absorption. As shown in **Fig.**
221 **4b**, the PL decays faster when poly-TPD or TFB is present on top of perovskite samples. We
222 propose that the luminescence quenching is caused by energy transfer from the perovskite to
223 low-energy states with charge-transfer character at the ZnO/poly-TPD (or TFB) interface. With
224 PVK or TPBi, no quenching is observed since their deeper highest occupied molecular orbital
225 levels raise the energy of the interfacial states above the perovskite bandgap (**Fig. 4c**). MSPE
226 can assemble between discontinuous perovskite grains as discussed above and provide a
227 physical spacer between ZnO and the hole-transport materials (**Fig. 4d**). As a result, none of
228 the hole-transport layers causes observable quenching of MSPE perovskites (**Fig. 4e, f**). The
229 existence of the spacer is further characterised as follows. SEM images of high magnification
230 (Supplementary Fig. 1) show that ZnO between perovskite grains in MSPE-based film is
231 covered by dark regions composed of organics with lower atomic numbers (Supplementary
232 Note 5). Increasing molar ratio of MSPE leads to increasing areal density of dark regions and
233 decreasing areal density of the perovskite grains, suggesting that the dark regions are MSPE.
234 The existence of the organic spacer in MSPE films is also consistent with AFM measurements
235 (Supplementary Fig. 8) as discussed before. A cross-section STEM-HAADF image of a half
236 device sample with a structure of ZnO/PEIE/MSPE-based perovskite/Au and associated
237 energy-dispersive X-ray spectroscopy (Supplementary Fig. 19) show that an organic layer of
238 MSPE fills the gaps between perovskite grains.

239
240 In this work, a multifunctional molecule MSPE was designed to control the optoelectronic,
241 crystal and morphological properties of perovskite films. MSPE improves crystallinity and
242 removes non-radiative dark regions in the perovskite films. Simultaneously, self-assembly of
243 MSPE between discontinuous perovskite grains removes interfacial quenching pathways in the
244 devices. Comprehensive suppression of non-radiative pathways in the films and devices allows
245 us to achieve efficient and bright perovskite LEDs with the best operating stability among

246 perovskite LEDs having EQE exceeding 20 % at high brightness. Our results suggest that low-
247 temperature solution-processable perovskite LEDs have the potential to achieve high efficiency
248 at high brightness and to surpass conventional LED technologies.

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250

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321 **Fig. 1: Perovskite LED structure and performance.**
322 **a**, Molecular structure of MSPE. **b**, STEM- HAADF image of a full MSPE LED. Scale bar:
323 200 nm. **c**, Ideal Lambertian profile and experimental angle-dependent emission data. **d**, Peak
324 EQE distribution of devices fabricated from precursors with different molar fractions of
325 MSPE/PbI₂. **e**, Current density versus voltage (black) and radiance versus voltage (red)
326 characteristics of the champion MSPE LED. **f**, EQE versus current density characteristics of
327 the champion device. Inset shows their EL spectra at different bias. **g**, Reported peak EQE and
328 peak radiance of various NIR LEDs according to the data provided in Supplementary Table 1,
329 3. **h**, Peak EQE (left) and peak radiance (right) histograms of 42 MSPE LEDs. **i**, Operational
330 stability measurement.

331

332 **Fig. 2: Characteristics of perovskite films and molecular interactions.**
333 **a**, GIWAXS patterns of perovskite films. **b**, Hyperspectral image of perovskite films. Scale
334 bar: 10 μm. **c**, SEM image at 5 kV (left) and the corresponding CL intensity map (right) of
335 the control and MSPE films. Scale bar: 400 nm. © Cambridge University Press; Reproduced
336 with permission from [34], © Microscopy Society of America 2022, published by Cambridge
337 University Press. **d**, XRD patterns of perovskite films. **e**, PLQE of perovskite films. **f**, FTIR
338 spectra of MSPE and perovskite precursors. **g**, ¹²⁷I NMR spectra. **h**, XPS spectra of Pb 4f. **i**,
339 FTIR spectra of MSPE molecules of different concentrations.

340

341 **Fig. 3: Charge-carrier kinetics of perovskite films.**
342 **a**, Confocal PL intensity (left) and lifetime (right) of the control films and **c** of MSPE films.
343 Scale bar: 5 μm. **b**, Recombination rate $dn(t)/dt$ against charge carrier density $n(t)$ of control
344 films and **d** of MSPE films.

345

346 **Fig. 4: Time-resolved photoluminescence decay kinetics of perovskites with charge-**
347 **transport layers.**
348 **a**, Schematic illustration of the control perovskite grains with charge-transport layers in a full
349 device and **d** of the MSPE-based perovskite grains. **b-c**, Time-resolved photoluminescence
350 decay kinetics of ZnO/PEIE/Control samples coated with different hole-transport materials
351 and **e-f** of MSPE samples.

352

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379 **Author contributions**

380 Y. S., L. C., and N. C. G. conceived the work. Y. S. developed efficient perovskite LEDs
381 under the supervision of L.C. and N. C. G. L. G. performed chemical synthesis, FTIR and
382 XPS under the supervision of L. C. L. D. performed TA measurements. Y. S. and L. D.
383 performed time-resolved PL measurements. C. C. performed confocal TCSPC measurements.
384 J. F. O and M. L. performed STEM-HAADF and EDS measurements under the supervision
385 of C. D. J. F. O performed SEM-CL measurements. K. J. performed hyperspectral imaging
386 measurements. S. J. Z. performed PDS measurements. A. J. M. performed GIWAXS
387 measurements. Y. L. performed DFT simulations. Y. Z. performed SEM measurements. L.
388 G., Y. W., K. G., and D. Y. performed NMR measurements. L. Z. performed AFM
389 measurements. J. H., J. L., E. M. T and S. D. S. assisted in interpreting results. Y. S. wrote
390 the manuscript, which was revised by L. C. and N. C. G. All authors contributed to the work
391 and commented on the paper.

392 **Methods**

393

394 **Materials**

395 All chemicals were purchased from Sigma Aldrich, unless otherwise stated. The perovskite
396 precursor solution was prepared by dissolving FAI (Greatcell Solar Materials), PbI₂ (Alfa
397 Aesar) and MSPE at a molar ratio of 2.7: 1: x ($x = 0 - 0.9$) in *N,N*-dimethylformamide (DMF)
398 to give an overall concentration of 7 wt%. Poly-TPD was purchased from 1-Materials. ZnO
399 nanoparticles were synthesised according to previously reported procedures³⁵. MSPE was
400 purchased from Fluorochem or synthesized and purified according to the method in previous
401 literature³⁶ with modifications described as follows. In a two-neck flask, 4-
402 (methylsulfonyl)phenylacetonitrile (3.9 g, 20 mmol, J&K Chemical) was dissolved in 30 mL
403 dehydrated THF under nitrogen atmosphere. The mixture was cooled to 0 °C for 10 minutes.
404 Then lithium aluminium hydride solution in THF (2.4 M, 8.3 mL, 20 mmol) was added drop
405 by drop in 10 minutes. After stirring under nitrogen for an hour, the reaction mixture was
406 carefully quenched by excess sodium sulfate decahydrate. The product was extracted with ethyl
407 acetate, and the combined organic layer was dried over anhydrous sodium sulfate. After
408 filtration and evaporation, the crude product was purified by column chromatography on silica
409 gel (eluent: hexane/ ethyl acetate = 7:3, v/v) and recrystallization from chloroform/methanol to
410 afford MSPE as solid (1.52 g, yield: 38%, purity: 99.5%). ¹H NMR (400 MHz, DMF-d₇): δ
411 8.08 (d, $J = 8.0$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 3.42 (s, 3H), 3.10 (m, 2H), 2.93 (m, 2H).

412

413 **PeLED fabrication and characterisations**

414 Pre-patterned ITO-coated glass substrates (10-15 Ω sq⁻¹, Kintec) were cleaned by ultrasonic
415 bath in detergent, water, acetone and isopropanol for 5 min, consecutively. Then the ITO
416 substrates were dried and treated by oxygen plasma etching (forward power 200 W, reflected
417 power 0 W, 10 min). ZnO nanoparticles were spin-coated on ITO substrates at 3000 RPM and
418 then annealed at 150 °C for 10 min. Subsequently, 0.45 wt% PEIE in 2-methoxyethanol
419 solution was spin-coated at 5000 RPM and annealed 100 °C for 15 min. The substrates were
420 transferred into a nitrogen-filled glovebox. The perovskite layer was deposited by spin-coating
421 precursor solution on ZnO/PEIE substrates at 3000 RPM for 60 s and then annealing at 100°C
422 for 10 min. On top of the perovskite layer, poly-TPD (14 mg ml⁻¹ in chlorobenzene) was spin-
423 coated at 3000 RPM for 40 s. Finally, 7 nm of MoO_x and 60 nm of gold were sequentially
424 evaporated as top electrodes through a shadow mask (active device area 4.5 mm²) at a pressure
425 of 5 × 10⁻⁶ mbar. All devices were encapsulated by epoxy with a glass cover for further

426 measurements. J - V - R characteristics were measured using a Keithley 2400 source-measure
427 unit and a calibrated silicon photodetector. The detailed methods have been published in a
428 previous article¹⁸. In short, an LED was connected with a Keithley 2400 source-measure unit
429 and the photodetector was placed on-axis in front of the LED. The current that flowed through
430 the LED was measured at a given voltage from zero bias to forward bias. Simultaneously, the
431 signal generated in the photodetector by the photons emitted by the LED was measured. The
432 LED metrics were calculated taking into account the responsivity of the photodetector, the
433 geometry of the setup and the EL spectrum. This measurement setup was previously cross-
434 checked independently with a third-party industrial laboratory and other research groups^{5,37-38}.
435 EL spectra were measured by an Andor iDus spectrograph with a Si array detector. Device
436 temperature and infrared images were recorded by Hti HT-H8 thermal imaging camera.
437 For operational lifetime measurement, an LED with glass-epoxy encapsulation was
438 connected with a Keithley 2400 source-measure unit, which provided a constant current, in
439 ambient environment at room temperature. A photodetector was used to collect the emitted
440 photons from the LED. At the beginning and the end of the measurement, the emission
441 spectra were measured by a spectrometer (Ocean Insight).

442

443 **STEM-HAADF**

444 Cross-sectional lamellae were cut and thinned to electron transparency (200 nm) using a FEI
445 Helios Nanolab Dualbeam FIB/SEM following a standard protocol. The lamellae were
446 directly transferred to a FEI Osiris TEM operated at 200 kV, minimising air exposure to less
447 than 2 min. To minimise beam damage, high-angle annular dark field images (STEM-
448 HAADF) were acquired using at a beam current of around 140 pA, dwell time of 30 ms /
449 pixel, camera length of 115 mm, and spatial sampling of 5 nm / pixel.

450

451 **Film characterisations**

452 A combination of 520 nm continuous-wave laser, an integrating sphere and an Andor iDus Si
453 detector was used to measure the steady-state PL and PLQEs³⁹. The excitation intensity was
454 tuned by a filter with a focused beam spot of ~ 0.3 mm². XRD data was collected by X-Ray
455 Bruker D8 under an ambient environment. Hyperspectral images of photoluminescence were
456 measured using a wide-field hyperspectral microscope (IMA VISTM, Photon Etc.) with a
457 calibrated low-noise silicon CCD camera. A 405 nm continuous-wave (CW) laser was used
458 as a photoexcitation source, and the emission image was re-focused using broadband PL
459 emission from the sample. The spectral measurements are performed by scanning the angle of

460 the grating relative to the emitted light from the sample to form images at each wavelength
461 which are stacked to form a 3D data cube with x and y as navigation axis and c as wavelength
462 axis.

463 SEM-CL maps were acquired in an Attolight Allalin 4027 Chronos SEM-CL at room
464 temperature under high vacuum. Beam focusing before each data acquisition was performed
465 away from the sample areas used for the measurements to prevent specimen damage. CL
466 maps were acquired using 5 kV acceleration voltage, 625 pA beam current, and 100 ms/pixel
467 acquisition time. These conditions were found to be the optimum to minimise detrimental
468 beam damage-related effects in the perovskite emission. CL maps were processed and
469 analysed in LumiSpy v.0.1.2⁴⁰. The artefacts caused by cosmic rays saturating the
470 spectrometer were removed, and the edges of each map were cropped out as they tend to
471 show edge effects and higher CL intensities.

472 The maps of PL intensity and lifetime were obtained using a confocal time-correlated single-
473 photon counting (TCSPC) setup (PicoQuant, MicroTime 200). A 509 nm pulsed laser (2.5
474 MHz, ~30 fJ) was focused onto the sample with a 100x objective. The emission signal was
475 collected by a TCSPC detector through the same objective. A 20 $\mu\text{m} \times 20 \mu\text{m}$ domain was
476 spatially scanned using a Galvano mirror system and confocal pinhole. The lifetime was
477 calculated from the slopes of the initial decay of the transient signal at each pixel.

478 GIWAXS data was collected at the I07 Surface and Interface Diffraction beamline at the
479 Diamond Light Source (Didcot, UK). The beam energy was 15 keV (0.82656 Å). The
480 scattered beam was collected by a Pilatus 2M large area detector, at a sample-detector
481 distance of 550 mm and calibrated with a lanthanum hexaboride (LaB₆) sample. The
482 incidence angle was kept at 0.3° to achieve bulk-preferential probing with a frame exposure
483 of 1 s. The sample chamber was continuously purged with a 1.5 L min⁻¹ He flow. Data was
484 processed with the DAWN software package.

485 Time-resolved photoluminescence spectroscopy was measured with an electrically gated
486 iCCD camera system (Andor iStar DH740 CCI-010) connected to a grating spectrometer
487 (Andor SR303i). The excitation fluence was estimated as 6 $\mu\text{J cm}^{-2}$.

488 SEM imaging was carried out at high vacuum ($< 4 \times 10^{-6}$ mbar) by a LEO GEMINI 1530VP
489 FEG-SEM system using 20 kV acceleration voltage. The surface morphology was collected
490 by a MFP-3D AFM System (Asylum/Oxford Instruments) in the ambient environment.

491

492

493 **Chemical interaction characterisations**

494 FTIR measurements were conducted by using a Fourier transform spectrometer (Nicolet
495 6700). The system was kept in a nitrogen atmosphere. Samples were prepared by potassium
496 bromide tableting method with background subtraction. XPS spectra were measured by a
497 monochromatic Al K α_1 X-ray source using a SPECS PHOIBOS 150 electron energy
498 analyser. ^{127}I NMR measurement was performed on Bruker AVANCE
499 NEO 400 MHz instrument. N, N-Dimethylformamide-d7 was used as solvent to prepare
500 samples for NMR measurement.

501

502 **Transient Absorption Spectroscopy**

503 All samples were given glass-lid encapsulation. The output of a Ti:sapphire amplifier system
504 (Spectra Physics Solstice Ace) operating at 1 kHz and generating ~ 100 fs pulses was used as
505 the fundamental laser. The 400-nm pump pulses were created by sending the 800-nm
506 fundamental beam of the Solstice Ace through a second harmonic generating (SHG) beta
507 barium borate (BBO) crystal (Eksma Optics). The broadband white probe was provided by
508 the Disco (Leukos Laser, STM-2-UV) and the pump-probe decay was controlled
509 electronically. The white light was split into two identical beams (probe and reference) by a
510 50/50 beamsplitter. The reference beam passing through the sample did not interact with the
511 pump, which allows for correcting for any shot-to-shot fluctuations in the probe that would
512 otherwise greatly increase the structured noise in the experiments. Based on this arrangement,
513 small signals with $\Delta T/T \sim 10^{-5}$ could be measured. The transmitted probe and reference pulses
514 were collected with a silicon dual-line array detector (Hamamatsu S8381-1024Q,
515 spectrograph: Andor Shamrock SR-303i-B) driven and read out by a custom-built board
516 (Stresing Entwicklungsbüro).

517

518 **LED measurement at pulsed mode**

519 Short square voltage pulses were generated by a HP8116A function generator and applied to
520 the device. A $5\ \Omega$ resistor was placed in series with the device. Transient voltages were
521 measured using a dual-channel oscilloscope (Agilent Technologies DSO6032A) and the
522 transient current was calculated from the voltage across the resistor in series with the
523 device⁴¹. A grating spectrometer (Andor SR303i) was used to collect electroluminescence
524 response of the device. Current and light output were averaged over 1500 pulses at each

525 voltage. The EQE was calibrated by comparing a DC response with that from the standard
526 EQE characterization setup.

527

528 **DFT simulations**

529 All DFT calculations were done using the Quantum Espresso suite (v7.0). The exchange
530 correlation was approximated by the PBE functional and the core-valence interactions were
531 treated using the ultrasoft pseudopotentials from the GBRV library. The electronic
532 wavefunctions were expanded in a plane wave basis with a cutoff of 40 Ry and charge-
533 density cutoff of 200 Ry, and the dispersion correction was included empirically using the
534 DFT-D3 method. The Brillouin zone of the bulk FAPbI₃ perovskite was sampled with a 6 × 6
535 × 6 Γ -centered Monkhorst-Pack \mathbf{k} -point grid, the atoms are relaxed until the Hellman-
536 Feynman force converges below 0.01 eV \AA^{-1} , and the volume until all components of the
537 stress tensor are below 10⁻² GPa. The passivated and unpassivated perovskite surfaces
538 without defects were created five atomic layers in the z -direction, and a vacuum spacing of 20
539 \AA was added to remove any spurious interactions. A commensurate 6 × 6 × 1 \mathbf{k} -point grid
540 was used to sample the Brillouin zone. For isolated ligands, a vacuum spacing of 20 \AA was
541 added in all 3 spatial directions and only the Γ point was sampled.

542 The binding affinity (E_{bind}) of the ligands to the perovskite surface was computed as

$$543 E_{\text{bind}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{ligand}}$$

544 where E_{tot} and E_{slab} are the total energies of the passivated and unpassivated perovskite
545 supercell, respectively, and E_{ligand} is the energy of the isolated ligand.

546

547 **Photothermal deflection spectroscopy**

548 Photothermal deflection spectroscopy measurements were performed in the transverse
549 configuration, utilising a probe beam from a 670 nm diode laser and a pump beam from a
550 tuneable light source consisting of a 250 W quartz tungsten halogen lamp and a 250 mm focal
551 length grating monochromator. The pump beam was mechanically chopped at 10 Hz and
552 passed to a vibration-isolated optical table through a fibre. The light-induced local heating of
553 the sample changing periodically the optical path of the probe beam was quantitatively
554 analysed with a quadrant Si photodiode, with the generated signal proportional to the material
555 absorbance demodulated with a lock-in amplifier (Stanford Research Systems SR830). The
556 perovskite samples, spin-coated on fused silica substrates (Spectrosil 2000), were immersed
557 in 3M Fluorinert FC-72 as the thermo-optic medium. For ZnO nanoparticles dispersed in

558 isopropyl alcohol, the measurement was done *in situ* by passing the probe beam through a
559 solution-filled quartz cuvette, with isopropyl alcohol serving as the medium.
560

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577 **Data Availability**

578 The data underlying this paper are available at the University of Cambridge repository
579 (<https://doi.org/10.17863/CAM.92711>).

580

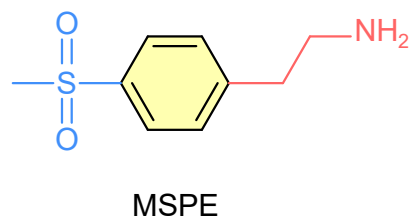
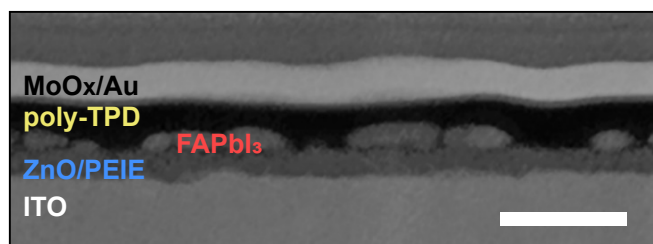
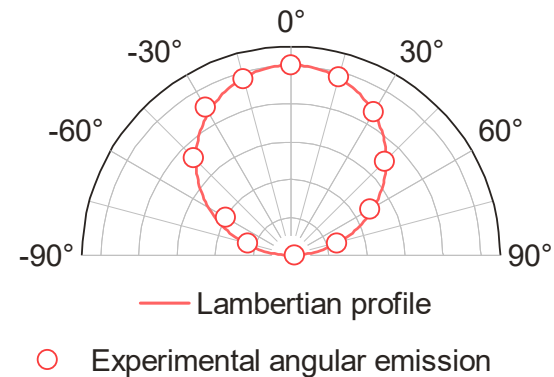
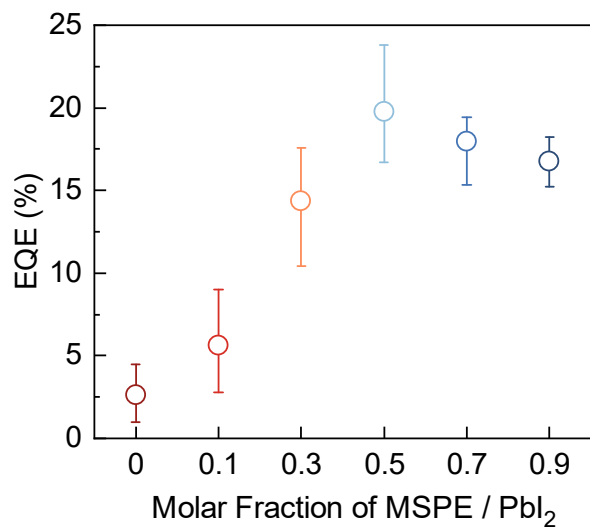
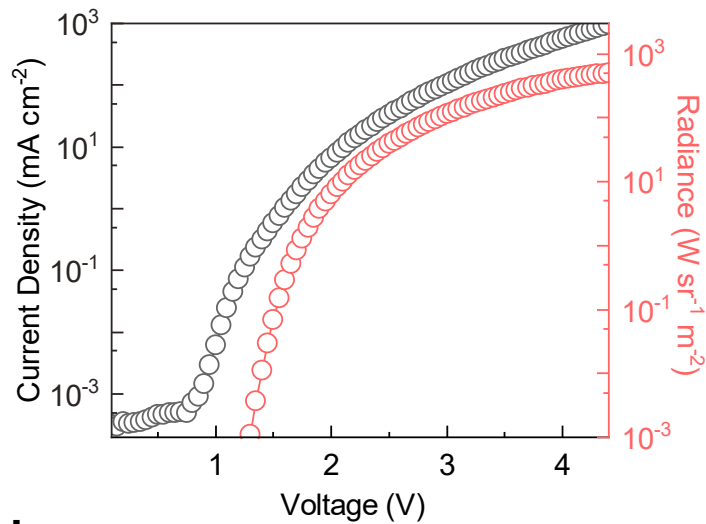
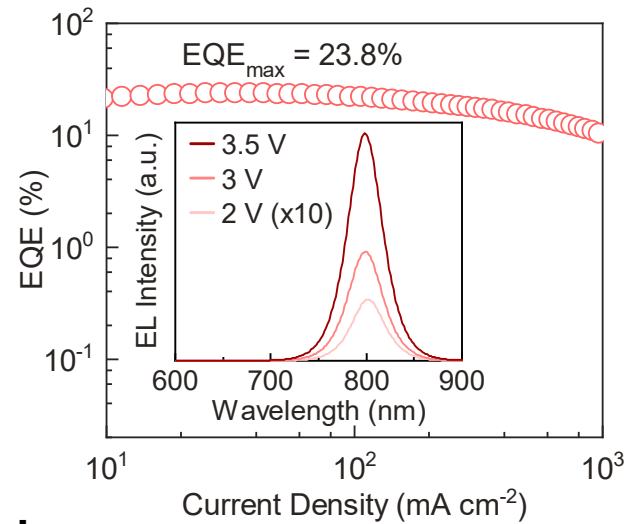
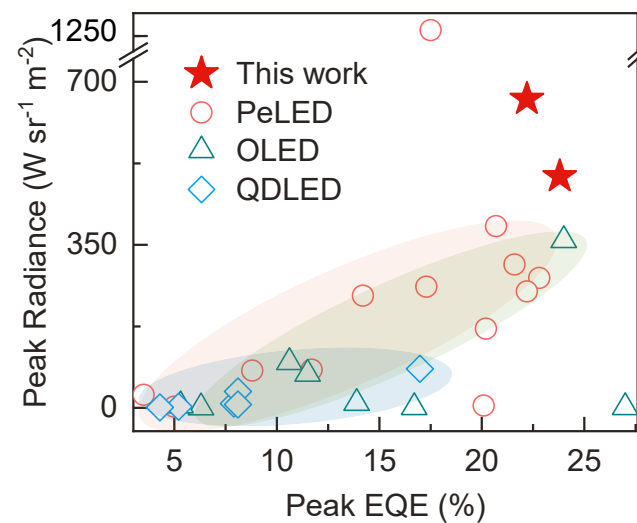
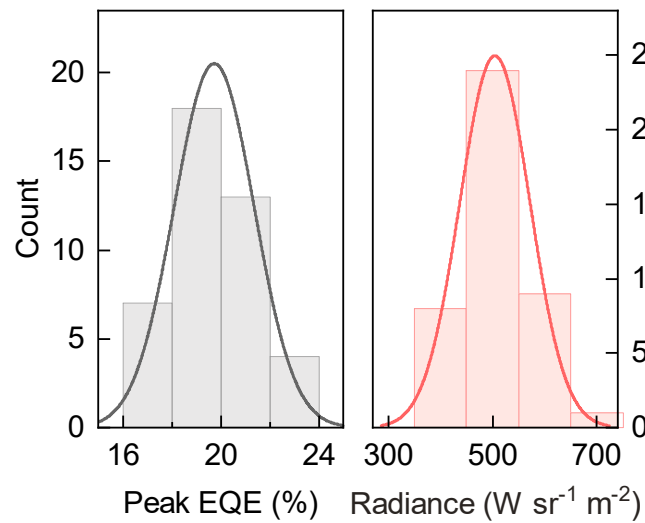
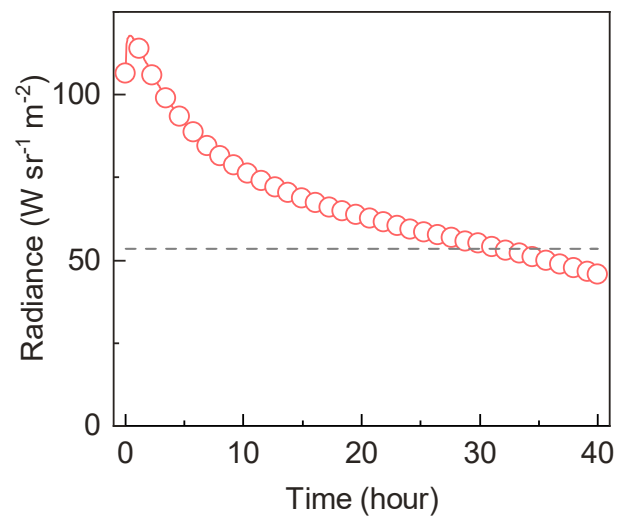
581 **Code Availability**

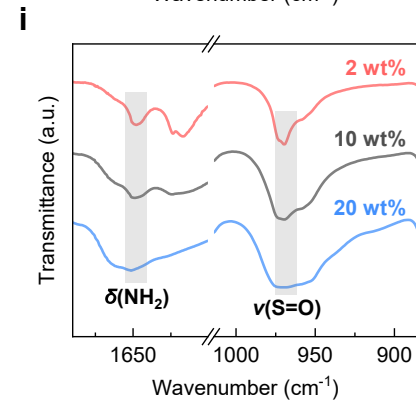
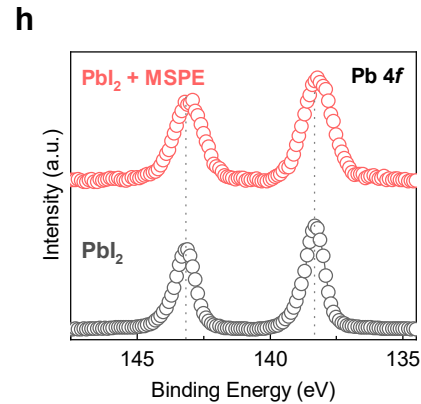
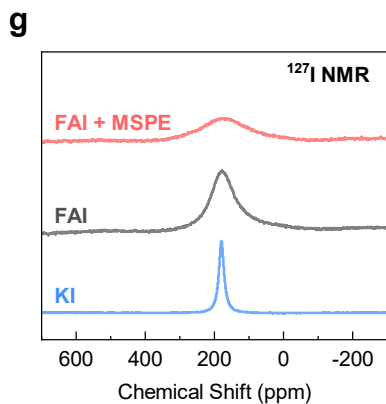
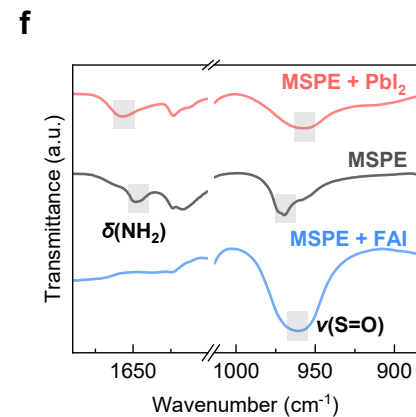
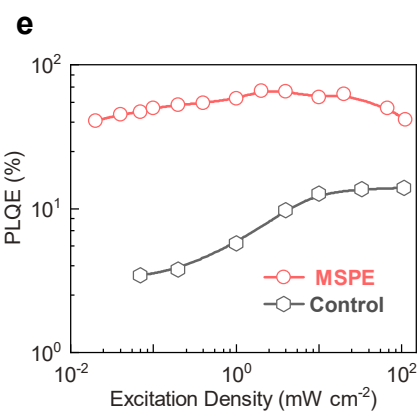
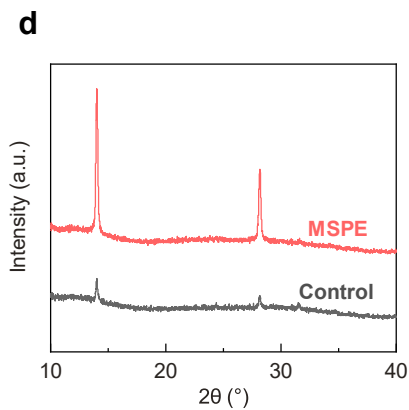
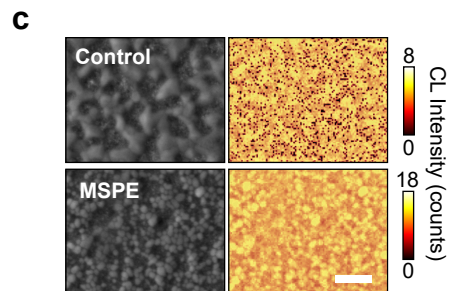
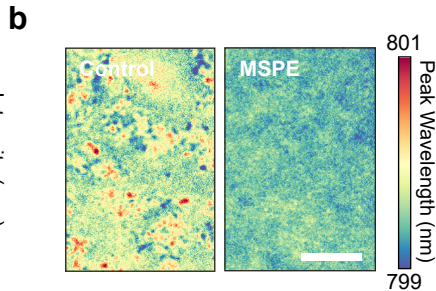
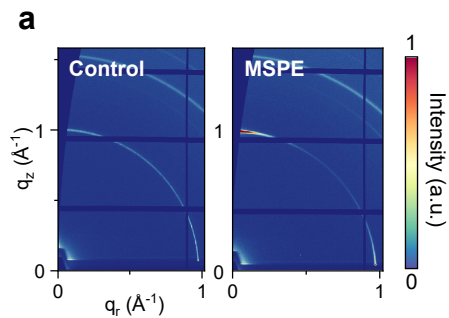
582 Not applicable.

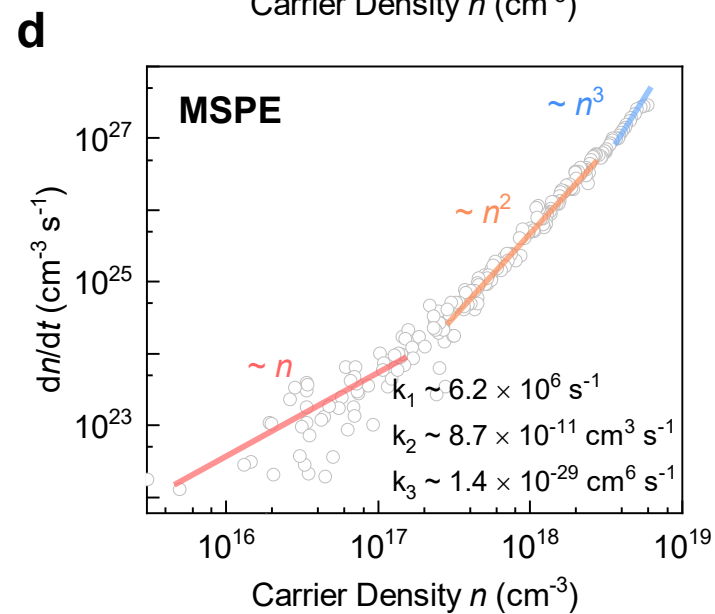
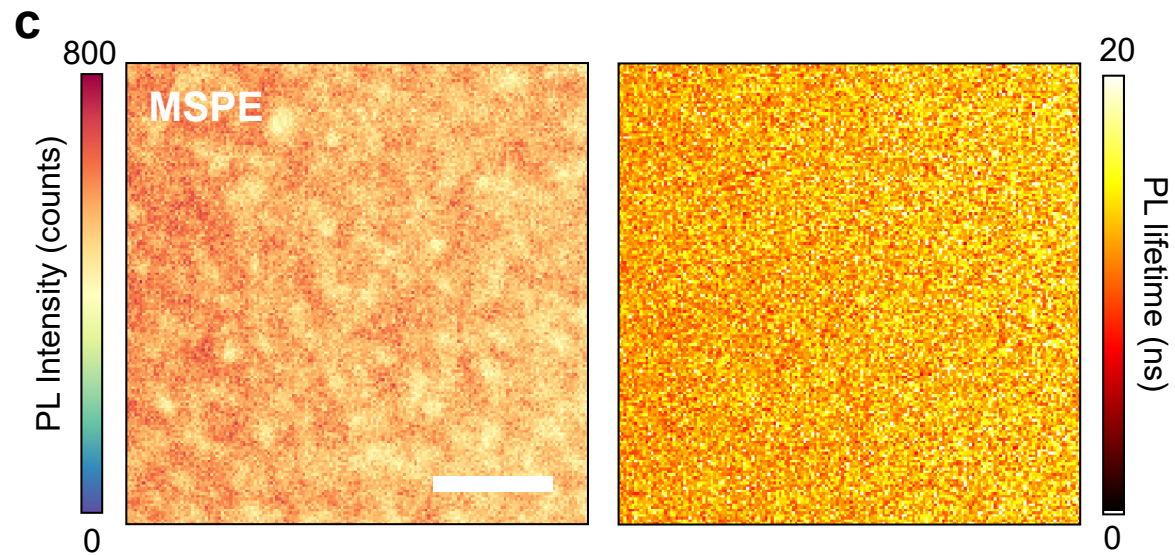
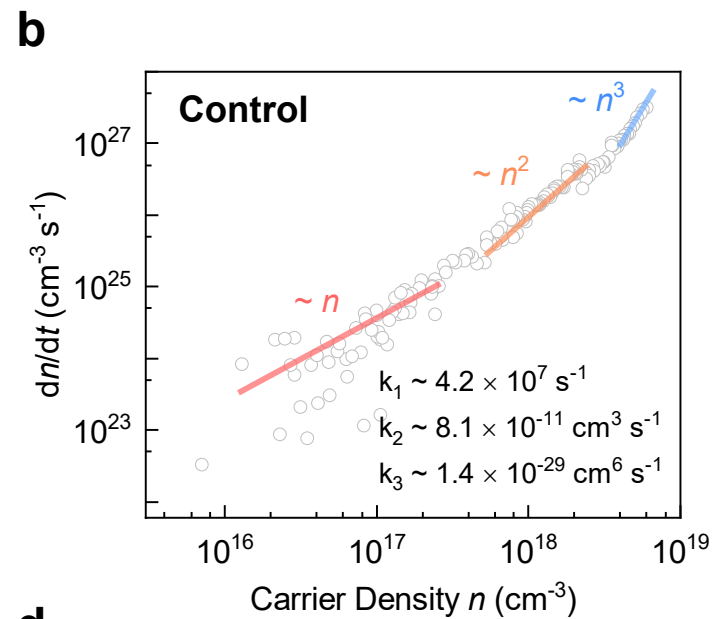
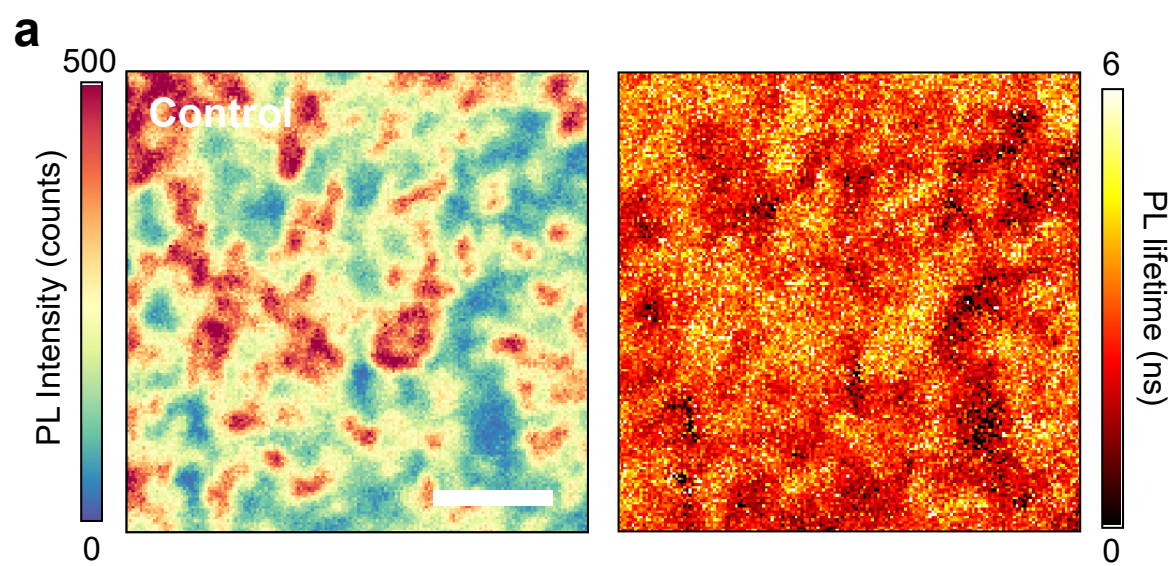
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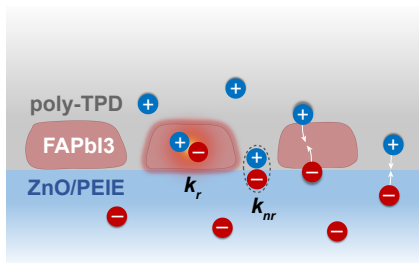
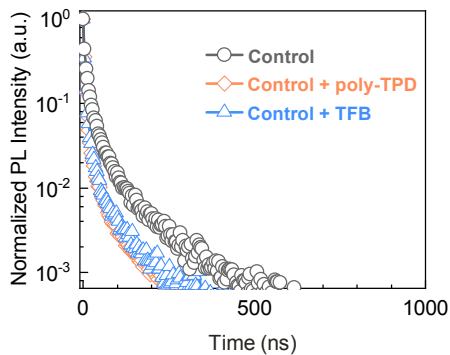
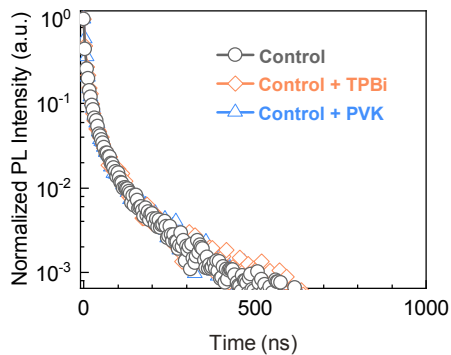
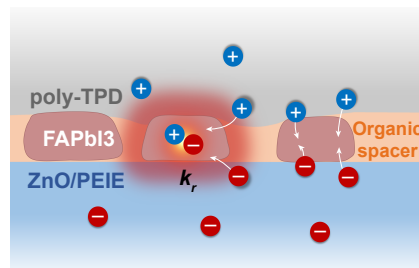
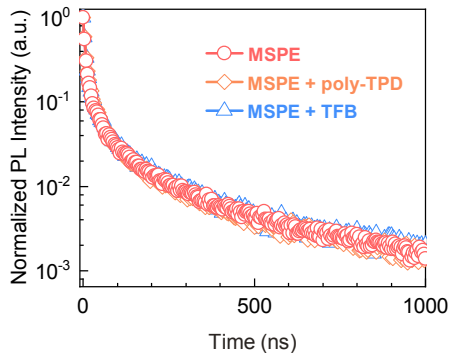
584 **Competing interests**

585 The authors declare no competing interests.

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a**b****c****d****e****f**