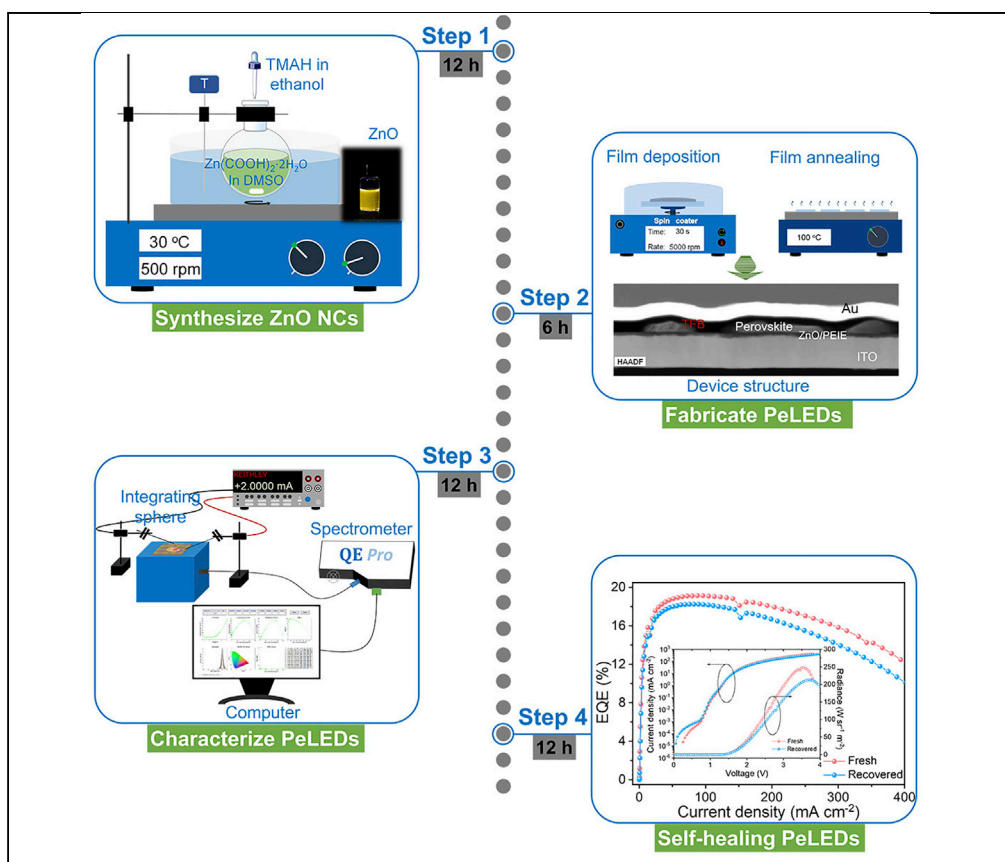


Protocol

Protocol for efficient and self-healing near-infrared perovskite light-emitting diodes



Yatao Zou,
Pengpeng Teng,
Zhongcheng Yuan,
..., Baoquan Sun,
Feng Gao, Weidong
Xu

bqsun@suda.edu.cn (B.S.)
ifewdxu@nwpu.edu.cn
(W.X.)

Highlights
A protocol to
fabricate efficient
near-infrared (NIR)
PeLEDs

Synthesis of high-
quality, electron-
transporting
materials of ZnO
nanocrystals (NCs)

Details on
characterization and
control of self-healing
properties of the
PeLED devices

Preparation of highly efficient and stable perovskite light-emitting diodes (PeLEDs) with reproducible device performance is challenging. This protocol describes steps for fabrication of high-performance and self-healing PeLEDs. These include instructions for synthesis of charge-transporting zinc oxide (ZnO) nanocrystals, step-by-step device fabrication, and control over self-healing of the degraded devices.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

Zou et al., STAR Protocols 3,
101631
September 16, 2022 © 2022
The Author(s).
[https://doi.org/10.1016/
j.xpro.2022.101631](https://doi.org/10.1016/j.xpro.2022.101631)



Protocol

Protocol for efficient and self-healing near-infrared perovskite light-emitting diodes

Yatao Zou,^{1,6} Pengpeng Teng,² Zhongcheng Yuan,² Jingcong Hu,³ Yue Lu,³ Baoquan Sun,^{1,4,*} Feng Gao,² and Weidong Xu^{5,7,*}¹Macao Institute of Materials Science and Engineering, Macau University of Science and Technology, Macau 999078, P. R. China²Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden³Beijing Key Laboratory of Microstructure and Properties of Solids, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, China⁴Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P. R. China⁵Frontiers Science Center for Flexible Electronics, Institute of Flexible Electronics (IFE), Northwestern Polytechnical University, Xi'an, China⁶Technical contact⁷Lead contact*Correspondence: bqsun@suda.edu.cn (B.S.), ifewdxu@nwpu.edu.cn (W.X.)
<https://doi.org/10.1016/j.xpro.2022.101631>

SUMMARY

Preparation of highly efficient and stable perovskite light-emitting diodes (PeLEDs) with reproducible device performance is challenging. This protocol describes steps for fabrication of high-performance and self-healing PeLEDs. These include instructions for synthesis of charge-transporting zinc oxide (ZnO) nanocrystals, step-by-step device fabrication, and control over self-healing of the degraded devices.

For complete details on the use and execution of this protocol, please refer to Teng et al. (2021).

BEFORE YOU BEGIN

The protocol below describes the specific steps to synthesize electron transport material of ZnO nanocrystals (NCs) and fabricate formamidinium lead tri-iodide (passivated with 2,2-[oxybis(ethyleneoxy)]diethylamine (ODEA)) based near-infrared PeLEDs. This protocol may also be suitable for fabricating PeLEDs with other perovskite emitters (e.g., bromide and iodide mixed perovskites) or with different passivation agents.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Dimethylsulfoxide (DMSO, anhydrous, ≥ 99.9%)	Sigma-Aldrich	Cas# 67-68-5
Dimethyl formamide (DMF, anhydrous, > 99.8%)	Sigma-Aldrich	Cas#68-12-2
Ethanol (anhydrous, >99.8%)	VWR	Cas#64-17-5
Ethyl acetate (anhydrous, 99.8%)	Sigma-Aldrich	Cas#141-78-6
Isopropyl alcohol (IPA, anhydrous, 99.5%)	Sigma-Aldrich	Cas#67-63-0
Ethanol amine (EA, ≥ 98%)	Sigma-Aldrich	Cas#141-43-5
Chlorobenzene (CB, anhydrous, 99.8%)	Sigma-Aldrich	Cas#108-90-7

(Continued on next page)



<i>Continued</i>		
REAGENT or RESOURCE	SOURCE	IDENTIFIER
Zinc acetate dihydrate (Zn(CH ₃ COOH) ₂ ·2H ₂ O, ≥ 98%)	Sigma-Aldrich	Cas#5970-45-6
Tetramethylammonium hydroxide pentahydrate (TMAH, ≥ 97%)	Alfa Aesar	Cas#10424-65-4
Formamidine iodide (FAI, ≥ 99.9%)	Greatcell solar	Cas#879643-71-7
Lead iodide (PbI ₂ , ultra dry, beads, 99.999%)	Alfa Aesar	Cas#10101-63-0
2,2-[oxybis(ethylenoxy)]diethylamine (ODEA, 98.0%)	Sigma-Aldrich	Cas#929-75-9
Polyethylenimine, 80% ethoxylated solution (PEIE, 37 wt.% in H ₂ O)	Sigma-Aldrich	Cas#26658-46-8
poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenyl-amine) (TFB, MW: 10,000–200,000)	American Dye Source, Inc.	ADS259BE
molybdenum oxide (MoO ₃ , 99.5%)	Alfa Aesar	Cas#1313-27-5
Gold pellet (Au, 99.999%)	Kurt J. Lesker Company	EVMAUX50G
Phenethylammonium iodide (PEAI, 98%)	Xi'an Polymer Light Technology. Corp.	Cas#151059-43-7
<i>Other</i>		
Centrifuge	Cence	H-1650
UV-ozone	Ossila Limited	L2002A1
Indium tin oxide (ITO) glass	Liaoning Youxuan New Energy Technology Co., Ltd	1.3 cm by 1.5 cm size; 0.7 mm thickness
PTFE hydrophilic membrane filters, 0.45 μm, 90 mm	VWR	Cat#28145-493
Spin-coater	POLOS	SPIN150i-NPP
Thermal evaporator	MBRAUN	PROvap-BR123
LED test system	Ocean Optics	QE Pro
Stability test system	Home-made	N/A

MATERIALS AND EQUIPMENT

PEIE and ODEA are stored in a fridge at ~8°C. TMAH, EA, Zn(CH₃COOH)₂·2H₂O, FAI, PbI₂, and solvents should be stored in a dry cabinet with relative humidity (RH) below 20%. The LED test system is home-built and placed in an N₂-filled glovebox (see schematic illustration in [Figure 6](#)), including a Keithley 2400 sourcemeter, a QE Pro spectrometer (Ocean Optics) and an integrating sphere (FOIS-1). This setup's absolute radiance and wavelength are calibrated by a visible-NIR light source (HL-3 PINT-CAL plus, Ocean Optics) and a mercury argon calibration source (HG-1, Ocean Optics).

Reagent	Final concentration	Amount
ZnO NCs in ethanol	~20 mg/mL	1 mL
PEIE in IPA	1.1 mg/mL	2 mL
30% ODEA-FAPbI ₃ in DMF	0.13 M	2 mL
PEAI in IPA	0.25 mg/mL	1 mL
TFB in CB	12 mg/mL	1 mL

The shelf life of ZnO NCs dispersion is around one month at 8°C. A longer storing time may result in aggregation of the ZnO NCs dispersion. PEIE, PEAi, and TFB solutions should be stored in an N₂-filled glovebox (O₂ < 1 ppm; H₂O < 1 ppm) and can be utilized within one week to get good performance. We suggest using freshly prepared perovskite precursor solutions within three days to achieve anticipated performance.

△ **CRITICAL:** DMSO, ethyl acetate, ethanol, IPA, and CB are flammable chemicals. EA is corrosive, and TMAH and PbI₂ are toxic. One should wear proper personal protective

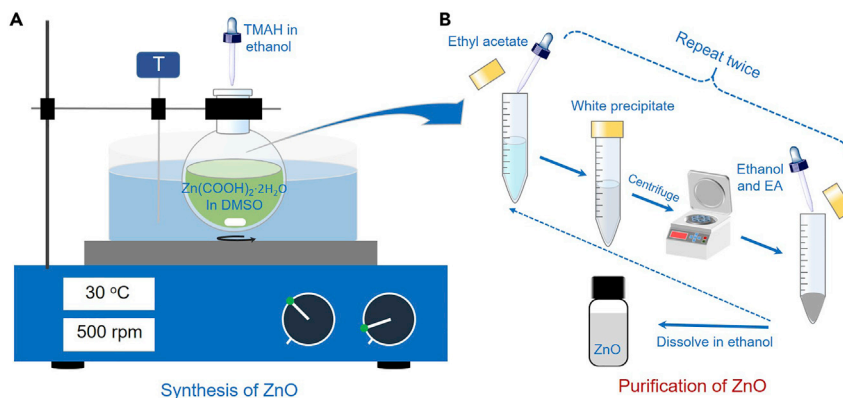


Figure 1. The steps of preparation of ZnO NCs

(A) Synthesis of ZnO NCs via hydrolysis reaction and condensation.
(B) Purification of ZnO NCs.

equipment (PPE) products (eye shields, face shields, and gloves) when using these chemicals in a well-ventilated fume hood or N_2 -filled glovebox.

Alternatives: The general chemicals (e.g., ethanol, IPA, DMSO, DMF, and CB) used in this protocol can be replaced by other sources. The instruments applied in this protocol can be replaced by those which have similar functions. For example, one can also use an O_3 -plasma to replace the UV-ozone to clean the ITO glass.

STEP-BY-STEP METHOD DETAILS

Preparation of ZnO NCs

⌚ Timing: 12 h

The synthesis of ZnO NCs here includes adding TMAH solution into a DMSO solution of zinc acetate dihydrate via hydrolysis reaction and condensation in the ambient. The following steps describe detailed processes of synthesizing ZnO NCs and consequent purification steps, as the schematic shown in [Figure 1](#).

1. Synthesis of ZnO NCs.
 - a. Add 335.9 mg zinc acetate dihydrate in 15 mL DMSO solution in a flask.
 - b. Heat and stir the solution at 30°C until completely dissolved.
 - c. Add 200 μ L of deionized water to the flask.
 - d. Dissolve 508.5 mg TMAH powder into 5 mL ethanol.
 - e. Add the TMAH solution into the flask dropwise within 5 min (e.g., 15 μ L per second).
 - f. Keep heating and stirring the solution at 30°C for another 12 h.

Note: By tuning the reactive raw materials and reaction time, the above method is also applicable for preparing magnesium-doped ZnO (ZnMgO) NCs, that is, another prevailing electron transporting material used in PeLEDs ([Zhao et al., 2018](#)).

2. Purification of ZnO NCs.
 - a. Transfer the obtained ZnO crude solutions to two centrifuge tubes (50 mL size) evenly.
 - b. Add about 20 mL ethyl acetate into each centrifuge tube to obtain white emulsion.
 - c. Centrifuge both tubes containing the emulsion at a relatively low centrifuge rate (the radius of the rotor is 12 cm) no more than 5,000 rpm, e.g., 3,000 rpm, for 3 min.

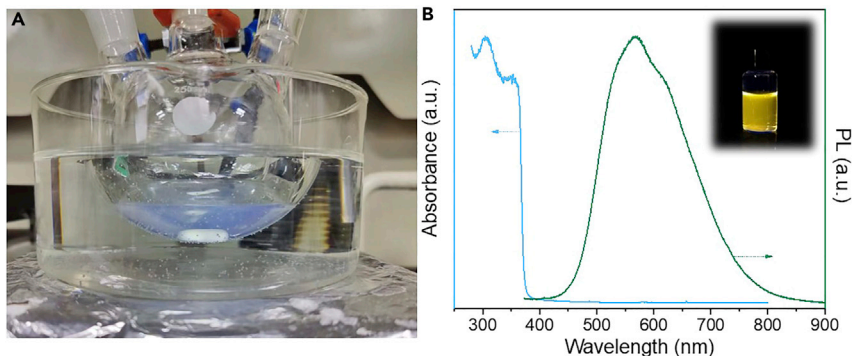


Figure 2. Characterization of the ZnO NCs solution

(A) Photograph of ZnO NCs crude solution after reaction at 30°C for 12 h.

(B) Photoluminescence (blue line) and ultraviolet-visible (UV-vis) absorption (green line) spectrum of the ZnO NCs solution. Insert shows the photograph of the ZnO NCs solution excited with a 365 nm UV lamp.

- d. Discard the supernatant.
- e. Add 2 mL ethanol in each centrifuge tube to dissolve the ZnO NCs before drying out (within 5 min).
- f. Introduce 10 μ L ethanolamine to the ZnO dispersion in each centrifuge tube.
- g. Repeat sub-steps 2b–f.

Note: When repeating the sub-steps 2b to 2f, the volumes of added ethyl acetate and ethanolamine change to 10 mL and 40 μ L for each centrifuge tube. Here, the ethanolamine mainly helps achieve a better dispersion and shelf stability of the ZnO NCs solution.

3. Disperse the obtained ZnO NCs in 8 mL ethanol in a glass vial after being filtered by a 0.45 μ m PTFE hydrophilic membrane filter.
4. Store the ZnO NCs dispersion at around 8°C, and warm up to room temperature before use.

△ CRITICAL: TMAH is a hazardous chemical. The “critical” note in the “materials and equipment” section describes its chemical properties and handling methods. The synthesis and purification steps should be conducted in an environment with RH lower than 40%. The stirring rate, adding rate of TMAH, and reaction temperature could dramatically influence the quality of the ZnO NCs. Figure 2 shows the fundamental characterizations of the ZnO NCs solution. The obtained crude NCs solution exhibits a light blue color because of its wide bandgap, as the UV-vis absorption spectra depicted in Figure 2B. It is noteworthy that the final ZnO NCs solution shows yellow photoluminescence (insert in Figure 2B) when excited with a 365 nm UV lamp, which mainly stems from its rich defects (i.e., oxygen vacancies) assisted emission.

Fabrication and characterization of perovskite light-emitting diodes

⌚ Timing: 6 h

The following steps describe detailed processes of depositing each functional layer of PeLEDs, which is illustrated in Figure 3.

5. Clean the patterned ITO glass substrates (thickness, \sim 0.7 mm; transmittance > 90%; square resistance, 7–9 Ω /sq) thoroughly to remove contamination on the surface. The detailed cleaning process involves ultrasonically treating (high power) the ITO glass substrates in detergent solution (e.g., Alconox detergent), deionized water, and ethanol bath in sequence for 20 min of each step.

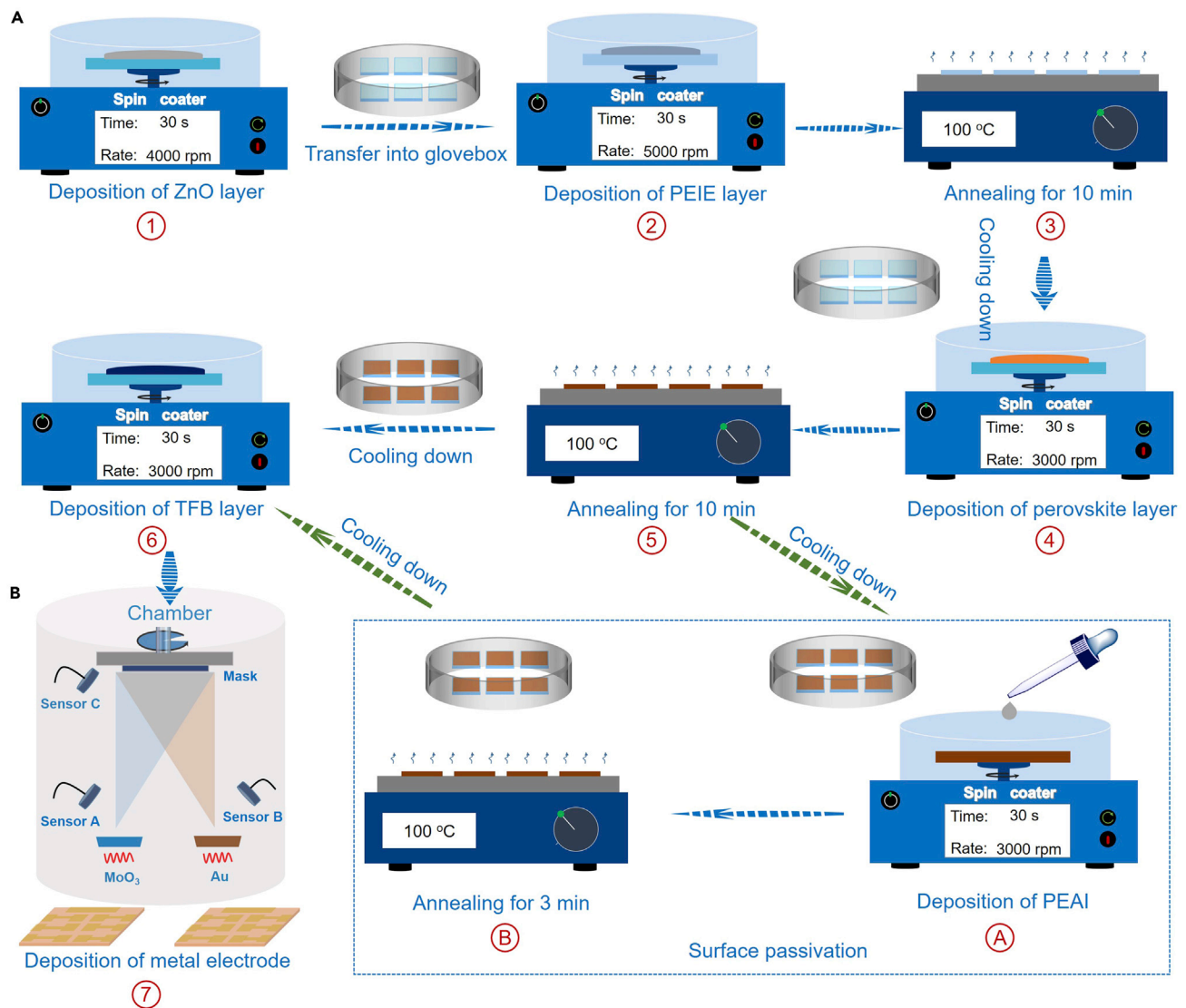


Figure 3. Steps for fabrication of PeLEDs

(A) Signed 1–6, deposition of the electron transport layer, perovskite layer, and hole transport layer; Signed A to B, surface passivation with PEAI (if applicable).

(B) Signed 7, deposition of MoO_3 and Au electrode in a thermal evaporator with a shadow mask.

6. Blow the ITO glass substrates with N_2 gas to remove residual solvents.
7. Place all the ITO glass substrates in a UV-ozone cleaner with ITO side upwards and treat them with UV-ozone for 20 min before use.

Optional: The cleaning method for ITO glass substrates may vary in different groups. For example, an alternative way is sonicating the ITO glass substrates in acetone, IPA, deionized water, and IPA in sequence. In addition to that, ITO glass substrates could also be cleaned with a detergent solution and subsequent TL-1 treatment (a mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume)) (Xu et al., 2019) at 85°C. In the case of UV-ozone treatment, O_3 -plasma treatment is also an alternative method to treat the ITO glass substrates.

8. Spin-coat 30 μL ZnO NCs solution on the ITO substrates at 4,000 rpm in a fume hood. The spin-coating process lasts 30 s for each. (Figure 3A-1).

Note: The RH in the fume hood dramatically influences the quality of ZnO layers. A low RH (20%–30%) is preferred to achieve high-efficiency PeLEDs with high reproducibility. This is mainly because the RH value impacts the surface chemistry of the ZnO layers, which plays a vital role in the subsequent crystallization of perovskite films.

9. Transfer the ZnO-coated substrates into an N₂-filled glovebox (O₂ < 1 ppm; H₂O < 1 ppm).
10. Spin-coat 50 μL PEIE (1.1 mg/mL) in IPA onto the ZnO-coated substrates at 5,000 rpm for 30 s (Figure 3A-2).
11. Bake the samples at 100°C for 10 min and wait for them to cool down to room temperature before the next step. (Figure 3A-3).
12. Prepare perovskite precursor solutions.
 - a. Dissolve 0.13 mmol of PbI₂, 0.26 mmol of FAI, and 0.039 mmol of ODEA are in 1 mL of DMF.
 - b. Stir the precursor at 60°C for 4 h.

Optional: The passivation agent ODEA could be alternatively replaced by 3, 6, 9, 12-tetraoxatetradecane-1, 14-diamine (Zou et al., 2021), 5-aminovaleric acid (Cao et al., 2018) and others with similar functionality. The stoichiometric ratio between different additives and perovskite and the peak EQE of the PeLEDs may vary due to the different passivation effectiveness of the additives as well as the perovskite film morphology.

13. Spin-coat 30 μL perovskite precursors at 3,000 rpm for 30 s onto the ZnO/PEIE coated substrates. (Figure 3A-4).
14. Bake the perovskite films at 100°C for 10 min before naturally cooling down to room temperature. (Figure 3A-5).
15. Surface passivation with PEAI (if applicable). (Figures 3A-A and 3A-B).
 - a. Deposit 50 μL PEAI (0.25 mg/mL in IPA) solution with a dynamic spin-coating process at 3,000 rpm for 30 s.
 - b. Bake the samples at 100°C for 3 min before cooling down to room temperature.

Alternatives: The surface passivation agent of PEAI could be replaced by phenylmethylammonium iodide, phenylbutan ammonium iodide (Guo et al., 2021), and triphenylphosphine oxide (Na Quan et al., 2020) or others showing similar chemical structures. The different chemicals may exhibit varied passivation effectiveness, therefore, the concentration of the passivation solutions should be carefully tuned to achieve excellent device performance.

△ CRITICAL: The atmosphere in the glovebox is of critical importance to the quality of the perovskite films. Solvents with high coordination affinity to PbI₂, such as DMSO and 1-methyl-2-pyrrolidinone (NMP), should be avoided in the glovebox. This is because the vapor residue of these solvents in the glovebox affects the intermediate phases as well as the crystallization dynamic of the perovskite films during the thermal annealing process. We show representative characteristics of the devices prepared in a DMSO-rich atmosphere in Figure 4. In addition, it is highly suggested to replace the contaminated aluminum foil (or wipe paper for removing solution residues in the spin-coater) as frequently as possible during spin-coating. Similarly, it is not desired to do the spin-coating and thermal annealing simultaneously, as the released solvent vapor alters the perovskite grain growth.

16. Spin-coat 30 μL TFB solution with a concentration of 12 mg/mL in CB at 3,000 rpm for 30 s (Figures 3A-6).

Potential: TFB could also be replaced by poly-TPD if the film thickness is optimized (Zhao and Tan, 2020).

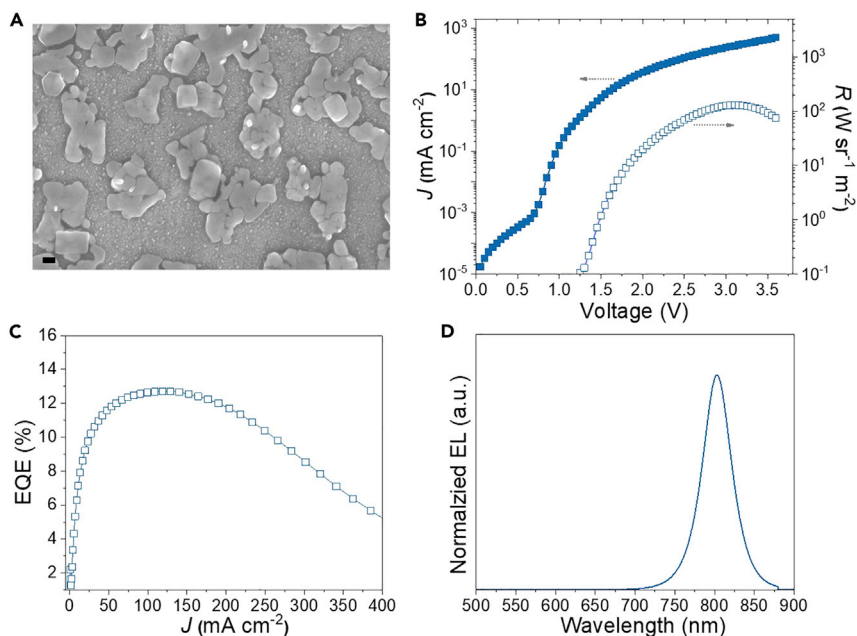


Figure 4. Device performance of PeLEDs fabricated in the spin-coater with a DMSO-rich atmosphere

See more detailed information on characterization of PeLEDs in step 19.

(A) SEM image of the perovskite film. The scale bar in the figure is 200 nm.

(B) Current density-voltage-radiance (J - V - R) curves.

(C) EQE-current density (EQE - J) curve.

(D) Electroluminescence spectra.

17. Load the samples into the vacuum chamber of a thermal evaporator.
18. Deposit MoO_3/Au electrode. (Figures 3B-7).
 - a. The vacuum chamber was pumped to a pressure below 2×10^{-6} mbar in 10 min.
 - b. Deposit 7-nm-thick MoO_3 at a rate of 0.2 \AA/s .
 - c. Deposit 5-nm-thick Au electrode at a rate of 0.2 \AA/s .
 - d. Sequentially deposit 55-nm-thick Au at a rate of 0.5 \AA/s .
 - e. The active area of PeLEDs is 7.25 mm^2 , defined by a shadow mask.

Note: The thickness of the ZnO/PEIE layer is about 20 nm, according to the cross-sectional STEM image shown in Figure 5. Discrete perovskite grains formed on the ZnO/PEIE surface are essential for improving the light outcoupling of the devices (Cao et al., 2018). These areas without perovskite films are covered by organic components, such as ODEA, which is capable of suppressing the leakage current.

19. Characterization of the PeLEDs in the N_2 -filled glove-box. Electrical outputs, such as current density-voltage-radiance (J - V - R) curves, EQE-current density curves (EQE - J), and EL spectra, were characterized by a home-built LED test system (Figure 6A).
 - a. Connect the anode and cathode with two probes of a Keithley sourcemeter.
 - b. Swept the PeLEDs from 0 to 4 V with an interval voltage of 0.05 V and 300 ms each step.
 - c. Measure the operational stability of the PeLEDs under a constant current density, such as 50 mA/cm^2 and 100 mA/cm^2 .

△ CRITICAL: An alternative test system, including a spectroradiometer (i.e., Photo Research 655), may also use to characterize the performance of PeLEDs, however, an integrating sphere coupled with a spectrometer is preferable to accurately measure the PeLEDs for the current case. The PeLEDs should be placed on the top of the integrating sphere and

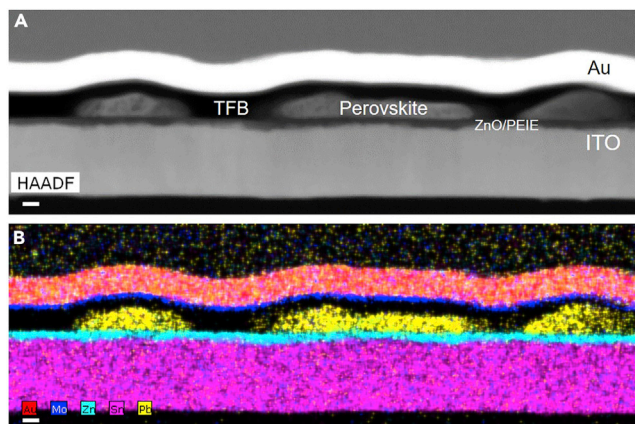


Figure 5. Cross-sectional scanning transmission electron microscopy (STEM) images of a FAPbI₃-based PeLED

The cross section of PeLED was acquired using focused ion beam method.

(A) STEM image of cross-section of a typical device that consists of ITO, electron transport layer of ZnO/PEIE, perovskite layer of ODEA based FAPbI₃, hole transport layer of TFB, and electrode of MoO₃/Au.

(B) The corresponding element dispersive X-ray (EDX) spectroscopy mapping image. Each element was clearly depicted by different color. Scale bars in the figures are 20 nm.

hence only the front light towards the pitch of the integrating sphere can be collected, as a schematic illustrated in [Figure 6A](#). In addition, the voltage intervals and dwell time of each step can influence the parameters of the PeLEDs due to initial trap filling, ion rearrangement, and/or device degradation once applied bias. Driving the devices at a constant current density is highly desired to accurately evaluate the device stability. In addition, to exclude the influence of luminance overshoot, a dwell time longer than 50 ms is necessary to give reliable results.

Self-healing process of perovskite light-emitting diodes

The following steps describe the detailed self-healing processes of moderately degraded PeLEDs by storing the devices in the N₂-filled glovebox or annealing at low temperature, as shown in [Figure 6B](#).

20. A sizeable current density of 100 mA/cm² was applied to measure the maximum EQE values and accelerate the device degradation to a half-operational lifetime (T₅₀).

△ **CRITICAL:** A large current density (e.g., > 300 mA/cm²) may lead to permanent damage to perovskite and/or organic charge transport layers. To make the self-healing process repeatable, a low current density (e.g., < 100 mA/cm²) for operation is desired.

21. Self-healing process of degraded PeLEDs.
 - a. Store the degraded devices in the glovebox at room temperature for a different duration.
 - b. The degraded devices could also be baked at a low temperature (such as 60°C) to accelerate the self-healing process.
22. Retest the maximum EQE and operational lifetime of the recovered PeLEDs.
23. Multiple-cycles of device aging and self-healing at room temperature.
 - a. Measure the PeLEDs with a constant current density of 10 mA/cm² for 12 h.
 - b. Rest the operated PeLEDs for 12 h.
 - c. Repeat the sub-steps 23a and b.

△ **CRITICAL:** Normally, the degraded devices could be directly stored in the glovebox to finish the self-healing process. However, a complex atmosphere (such as DMSO rich) in the glovebox may damage the devices simultaneously. In this case, one may use epoxy and

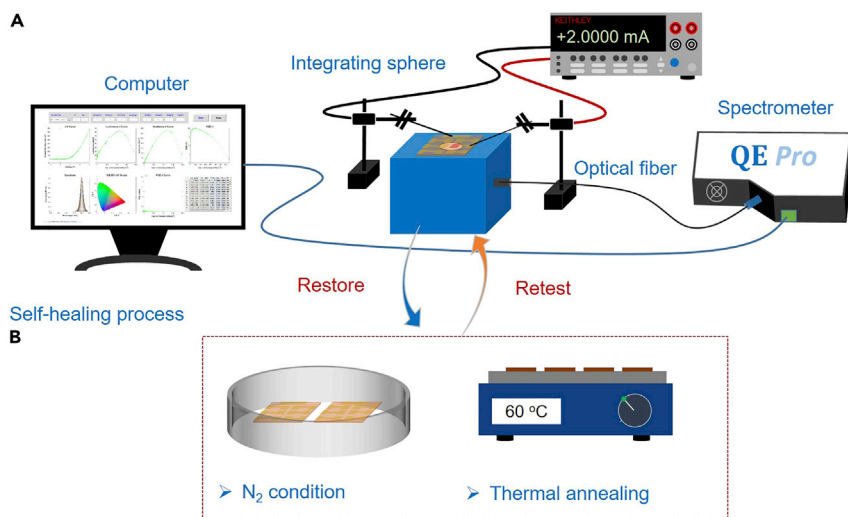


Figure 6. Self-healing process for the half-degraded PeLEDs

(A) Schematic illustration of the home-built LED test system, which mainly include an integrating sphere, a 2400 Keithley sourcemeter, a QE Pro spectrometer, a computer, and an optical fiber linked the spectrometer and the integrating sphere.

(B) Self-healing of the half-degraded PeLEDs via storing in an N₂-filled glovebox or baking at a low temperature.

glass slides to encapsulate the devices or store the devices in a vacuum chamber to make the devices self-repairable.

EXPECTED OUTCOMES

The fabricated near-infrared PeLEDs exhibit an emission wavelength of 800 nm. The maximum EQE and radiance of the champion devices could reach 20% and 250 W sr⁻¹ m⁻², respectively. Under a constant current of 50 mA/cm², an operational lifetime (T₅₀) could exceed 24 h. The half-degraded PeLEDs can recover their initial value after being stored in the glovebox for more than one week or baking at 60°C for 30 min. See detailed device performance in [Figure 7](#).

LIMITATIONS

This protocol should be applied carefully as there are potential limitations. Various external parameters have significant impacts on the fabrication process. Therefore, the performance of the fabricated PeLEDs is prone to sample-to-sample, batch-to-batch, and user-to-users variability. For example, high-quality ZnO NCs and the corresponding electron transport layer are essential to achieving efficient PeLEDs. The synthesis, purification, and deposition processes for the ZnO NCs should be conducted in the air under low humidity conditions. Ethanol and ethyl acetate should be anhydrous and carefully stored. In addition, the deposition and crystallization process of the perovskite films are equally crucial to the performance of the resultant PeLEDs. For example, during the film deposition process (steps 13 and 14), the atmosphere in the glovebox is highly relevant to the quality of the perovskite films ([Figure 8](#)). The intermediate phases and δ-FAPbI₃ may coexist in the perovskite films, limiting the device's performance. The self-healing may not work effectively in PeLEDs with Ag or Al as the metal electrode because both of them can migrate into the perovskite layer during storage or operation, and hence deteriorate the perovskite films permanently. This protocol is also applicable for demonstrating other iodide-based (such as CsPbI₃, FA_xCs_{1-x}PbI₃, and MA_xCs_{1-x}PbI₃ ([Xu et al., 2021](#))) efficient red or near-infrared PeLEDs. However, when bromide- and chloride-based perovskite emitters are selected to fabricate blue and green PeLEDs, severe photoluminescence quenching or perovskite decomposition could be observed, leading to inferior device performance ([Bai et al., 2022](#)). This is mainly ascribed to bromide- and chloride-based ammonium easily undergo decomposition on the alkaline ZnO/PEIE surface, and the bromide- and

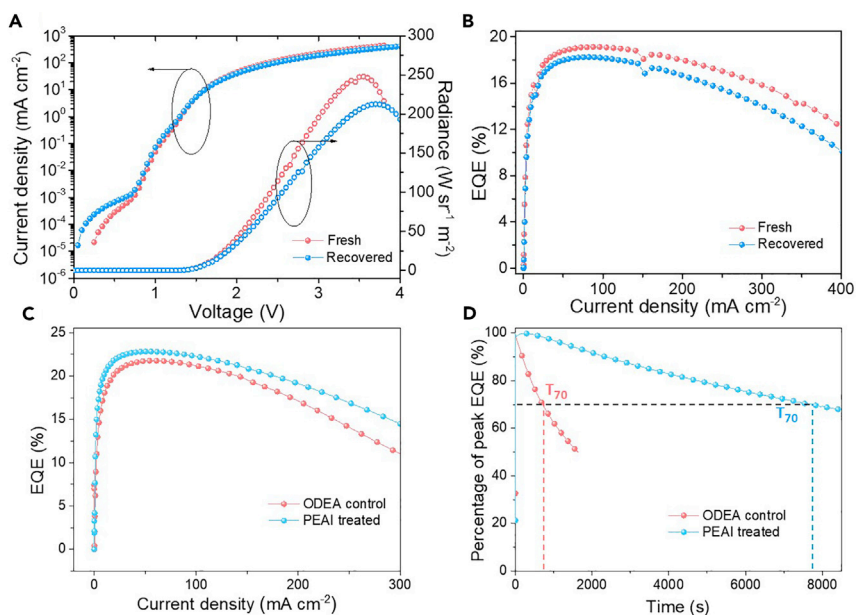


Figure 7. Device performance

(A) J-V-R curves of fresh and self-healed PeLEDs.

(B) EQE-J curve of fresh and self-healed PeLEDs.

(C) EQE-J curve of ODEA control and PEAI passivated PeLEDs.

(D) Operational lifetime of ODEA control and PEAI passivated PeLEDs. Reproduced with permission from (Teng et al., 2021).

chloride-based perovskite crystallize faster than their iodide-based counterparts, both of which could generate amount of defects within the perovskite films.

TROUBLESHOOTING

Problem 1

The ZnO precursor solution becomes cloudy once adding TMAH solution in step 1e.

Potential solution

Controlling the dropwise rate of the TMAH solution into the Zn(CH₃COOH)₂·2H₂O solution is an essential step in acquiring high-quality ZnO NCs for NIR PeLEDs. In this regard, slowing down the dropwise rate (e.g., 15 μL per second) and/or accelerating the stirring speed is helpful.

Problem 2

Very few amounts of ZnO NCs are obtained after centrifugation in step 2c.

Potential solution

Optimize the amount of ethyl acetate added to the ZnO solution before centrifugation. One can observe that the ZnO solution turns to white emulsion when enough ethyl acetate was added, however, the white emulsion may disappear when shaking the tube due to the redissolution. In this case, the optimal amount of the ethyl acetate should allow to obtaining enough white emulsion.

Problem 3

The ZnO nanocrystals could not be well dissolved in ethanol during or after the purification process (step 2e).

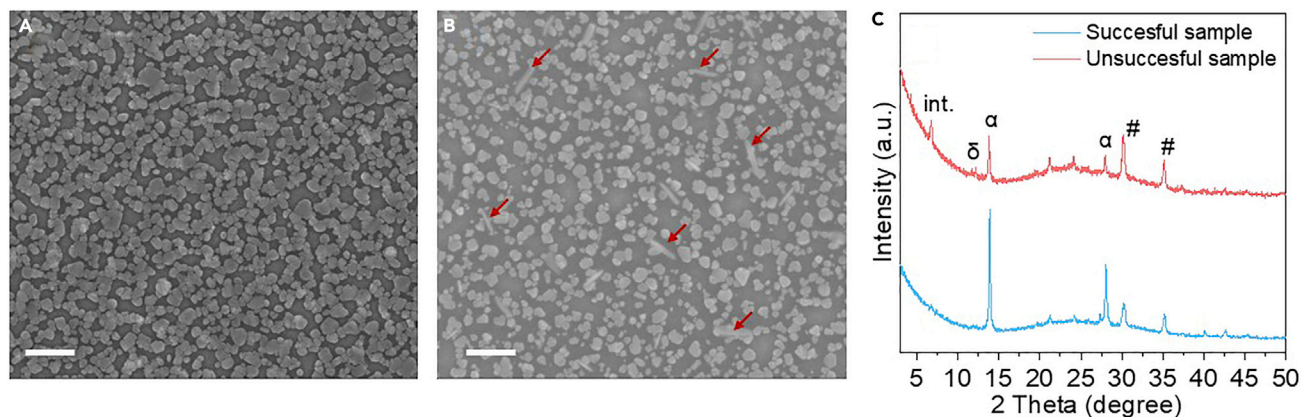


Figure 8. Comparison between successful and unsuccessful perovskite samples

(A) SEM images of the successful film that consists of perovskite domains with relatively uniform size distribution.

(B) SEM image of the unsuccessful film that with tiny perovskite crystals and perovskite nanoplates, as depicted by the red arrows in Figure 8B.

Scale bars in the figures are 1 μ m.

(C) XRD spectra. α , δ , and int. denote the diffraction from α -FAPbI₃, δ -FAPbI₃, and intermediate phase, respectively; # denotes the diffraction from PEIE/ZnO/ITO substrates.

Potential solution

After centrifuging, adding ethanol to dissolve the obtained ZnO NCs within 1 min, seriously avoiding the ZnO sediments aggregation. In addition, do not shake the centrifuge tubes violently after adding ethanol to accelerate the dissolution of ZnO NCs. Or reducing the amount of water addition (step 1c) or shortening the reaction time.

Problem 4

When depositing the ZnO films in ambient conditions with high humidity (step 8), PeLEDs with high EQE may also be achieved, but a severe EQE roll-off is expected (Figure 9).

Potential solution

Bake the ZnO films in the glovebox at 100°C for 10 min before the next step.

Problem 5

The perovskite films show rough film morphology after the thermal annealing process (step 14), and PeLEDs based on them demonstrate inferior device performance (Figure 4).

Potential solution

Purge the glovebox for 30 min before starting any film deposition. In addition, the maximum storage time for perovskite precursor solutions is up to one week. Prepare a new precursor solution if the precursors are stored for more than three days.

Problem 6

Particles are visible after TFB spin-coating (step 16).

Potential solution

Filter the TFB and perovskite solution, or prepare a fresh one instead.

Problem 7

The reproducibility of PeLEDs is poor from batch to batch.

Potential solution

Reduce the maximum number of devices from one batch. In addition, fully purge the chamber of the spin-coater before depositing different solutions.

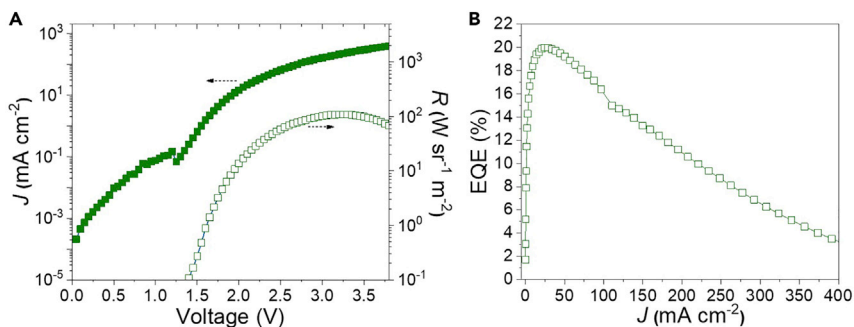


Figure 9. Device performance of PeLEDs with ZnO deposited in air with high humidity

(A) J-V-R curves.

(B) EQE-J curve.

Problem 8

The efficiency of degraded PeLEDs cannot recover after being stored for a long time (step 22).

Potential solution

Keep in mind that not every device can restore its initial performance as the damages of charge transport layers and corrosion of electrodes are unrecoverable. Using Au as the electrode improves the stability of PeLEDs as it shows minimum metal ion diffusion into perovskite layers and the best chemical robustness compared to Al or Ag.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Weidong Xu (jfewdxu@nwpu.edu.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

No data or code was generated in this study.

ACKNOWLEDGMENTS

We acknowledge the support from the ERC Starting Grant (no. 717026), the Swedish Energy Agency Energimyndigheten (no. 48758-1), and the Swedish Government Strategic Research Area in Materials Science on Functional Materials Linköping University (Faculty Grant SFO-Mat-LiU no. 2009-00971). Y.Z. and B.S. also thank the support from Macau SAR (file no. 0044/2021/A).

AUTHOR CONTRIBUTIONS

W.X. conceived the idea and supervised the study. Y.Z., P.T., J.H., and Z.Y. conducted the experiments and analyze the data. Y.Z. and W.X. drafted the manuscript. F.G., S.B., and Y.L. provide the insights. All the authors provided revisions to the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Bai, G., Zou, Y., Li, Y., Cai, L., Chen, B., Zang, J., Hong, Z., Chen, J., Chen, Z., Duhm, S., et al. (2022). Revealing a zinc oxide/perovskite luminescence quenching mechanism targeting low-roll-off light-emitting diodes. *J. Phys. Chem. Lett.* *13*, 3121–3129.
- Cao, Y., Wang, N., Tian, H., Guo, J., Wei, Y., Chen, H., Miao, Y., Zou, W., Pan, K., He, Y., et al. (2018). Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures. *Nature* *562*, 249–253.
- Guo, Y., Apergi, S., Li, N., Chen, M., Yin, C., Yuan, Z., Gao, F., Xie, F., Brocks, G., Tao, S., and Zhao, N. (2021). Phenylalkylammonium passivation enables perovskite light emitting diodes with record high-radiance operational lifetime: the chain length matters. *Nat. Commun.* *12*, 644.
- Na Quan, L., Ma, D., Zhao, Y., Voznyy, O., Yuan, H., Bladt, E., Pan, J., Garcia de Arquer, F.P., Sabatini, R., Piontkowski, Z., et al. (2020). Edge stabilization in reduced-dimensional perovskites. *Nat. Commun.* *11*, 170.
- Teng, P., Reichert, S., Xu, W., Yang, S.-C., Fu, F., Zou, Y., Yin, C., Bao, C., Karlsson, M., Liu, X., et al. (2021). Degradation and self-repairing in perovskite light-emitting diodes. *Matter* *4*, 3710–3724.
- Xu, W., Hu, Q., Bai, S., Bao, C., Miao, Y., Yuan, Z., Borzda, T., Barker, A.J., Tyukalova, E., Hu, Z., et al. (2019). Rational molecular passivation for high-performance perovskite light-emitting diodes. *Nat. Photonics* *13*, 418–424.
- Xu, Y., Xu, W., Hu, Z., Steele, J.A., Wang, Y., Zhang, R., Zheng, G., Li, X., Wang, H., Zhang, X., et al. (2021). Impact of amine additives on perovskite precursor aging: a case study of light-emitting diodes. *J. Phys. Chem. Lett.* *12*, 5836–5843.
- Zhao, B., Bai, S., Kim, V., Lamboll, R., Shivanna, R., Auras, F., Richter, J.M., Yang, L., Dai, L., Alsari, M., et al. (2018). High-efficiency perovskite–polymer bulk heterostructure light-emitting diodes. *Nat. Photonics* *12*, 783–789.
- Zhao, X., and Tan, Z.-K. (2020). Large-area near-infrared perovskite light-emitting diodes. *Nat. Photonics* *14*, 215–218.
- Zou, Y., Teng, P., Xu, W., Zheng, G., Lin, W., Yin, J., Kobera, L., Abbrent, S., Li, X., Steele, J.A., et al. (2021). Manipulating crystallization dynamics through chelating molecules for bright perovskite emitters. *Nat. Commun.* *12*, 4831.