

Supporting Information

Spectral stable blue light-emitting diodes via asymmetric organic diamine based Dion-Jacobson perovskites

Yuqiang Liu,^{1,2} Luis K. Ono,¹ Guoqing Tong,¹ Tongle Bu,¹ Hui Zhang,¹ Chenfeng Ding,¹ Wei Zhang,¹ Yabing Qi^{1,*}

¹ Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa 904-0495, Japan

² College of Textiles & Clothing, Qingdao University, Qingdao, 266071, China

*Corresponding author: Yabing Qi, E-Mail: Yabing.Qi@OIST.jp

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1. Experimental section

Materials

PEDOT:PSS (Clevios PVP AI 4083) was purchased from Heraeus. DPDABr₂ was purchased from TCI. Poly (sodium 4-styrenesulfonate) (PSSNa, M_w~70000), PbBr₂ (99.999%), PbCl₂ (99.999%) and CsBr (99.999%) were purchased from Sigma-Aldrich. 18-Crown-6 (Crown) and DMSO were purchased from Wako. TPBi and Liq were purchased from Luminescence Technology. All reagents in this work were used as received without further purification.

Perovskite precursor preparation

CsBr (0.22 mmol), PbBr₂ (0.1 mmol), PbCl₂ (0.1 mmol), crown (0.014 mmol) and DPDABr₂ (from 0 to 0.06 mmol) were mixed in 1 mL DMSO, stirred for 5 h and filtered by a 0.22 μm filter. The temperature of the perovskite precursor solution was kept at 70 °C before the spin-coating process. The spin-coating process was carried out at 1000 rpm for 5 s and then 4000 rpm for 55 s. The deposited film was annealed at 60 °C for 5 min and then at 100 °C for 5 min. The whole process was performed in a dry N₂ glovebox with a relative humidity <10 ppm.

PEDOT:PSS solution preparation

The final PEDOT:PSS solution was obtained by mixing the PEDOT:PSS (AI 4083) aqueous solution with the PSSNa aqueous solution (100 mg/mL) by a volume ratio of 6:5. After being stirred for 30 min, the solution was filtered by a 0.45 μm filter. The solution was spin-coated at a speed of 6000 rpm for 1 min, followed by annealing at 145 °C for 30 min.

Device fabrication

The PEDOT:PSS solution was spin-coated onto the pre-cleaned ITO substrates. Perovskite films were deposited onto the PEDOT:PSS films. After that, 40 nm TPBi, 2 nm Liq and 100

nm Al were evaporated onto the perovskite films by a thermal evaporator. The active area of the devices is 0.04 cm².

Characterization

The absorption curves were recorded by a UV-vis spectrophotometer (JASCO V-670). Steady-state PL curves were collected by a spectrophotometer (JASCO FP-8500, excitation wavelength = 360 nm, sensitivity PMT voltage = 350 V). PLQY values were measured by a spectrophotometer (JASCO FP-8500) with an integrating sphere. Time-resolved PL spectra were collected by a time-resolved spectrometer (Hamamatsu, Streakscope) with an excitation wavelength of 400 nm from a femtosecond mode-locked Ti:sapphire laser. The CLSFM images of the perovskite films were mapped by Leica laser scanning confocal fluorescence microscopy with an exciting laser at 405 nm. In the CLSFM system, the focused laser scans the objective (perovskite films in this case) point by point. Fluorescence emission by each point of the perovskite films will be received by the detector. Based on the detector signal, a real photograph can be reconstructed. The fluorescence intensity is the information acquired by the system. The color can be changed by the CLSFM software. Because the green color is more sensitive to human eyes, the CLSFM software usually sets green color as default. XRD patterns were recorded by a Bruker D8 Discover diffractometer (Bruker AXS, Cu X-ray source). The morphology of the perovskite films was examined by SEM (Hitachi, S-3000N). XPS (Al-K α = 1486.6 eV) and UPS (He-I α = 21.22 eV) spectra were collected by a photoelectron spectrometer (AXIS Ultra HAS, Kratos). The binding energy scales for UPS and XPS were calibrated by measuring the Fermi edge (E_F = 0 eV) and Au 4f_{7/2} (84.0 eV) on a clean Au surface. The energy resolutions for UPS and XPS extracted from the clean Au were 0.14 and 0.7 eV,

respectively. UV and X-ray induced damages were examined by taking five consecutive spectra and comparing those spectra. If no changes were observed, these five spectra were averaged to a single spectrum. The current-voltage characteristics (Figure S9) of perovskite films are measured under light illumination of ~ 10 mW/cm². All device characterizations were performed at room temperature with encapsulation by a UV glue (Norland NOA61). Optoelectronic characterizations were measured by a spectroradiometer (Konica Minolta CS-2000) with a Keithley 2400 source-meter. The interval of applied bias is 0.5 V. The scanning duration for each bias point is 2.5 s.

2. Supplementary Figures

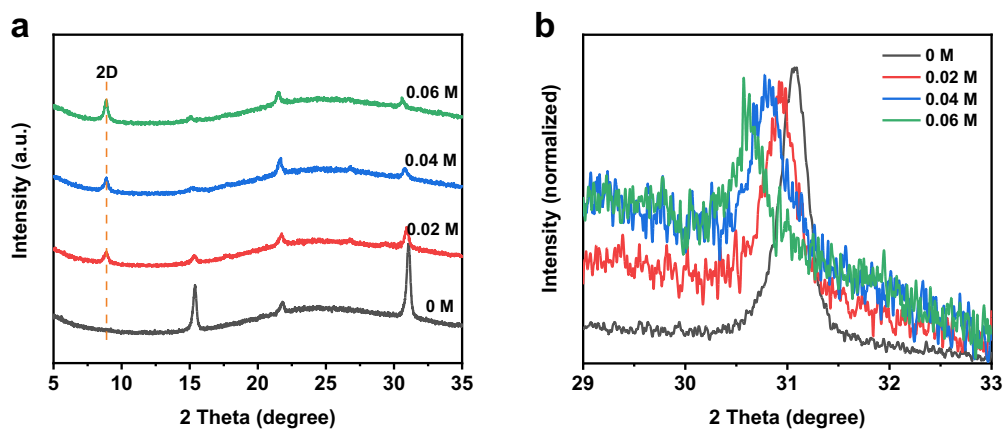


Figure S1. (a) XRD patterns of the CsPb(Br/Cl)₃ perovskite films with different DPDA concentrations (0 M, 0.02 M, 0.04 M and 0.06 M); (b) Normalized XRD patterns of the 3D perovskite within the diffraction peaks of 29~33°.

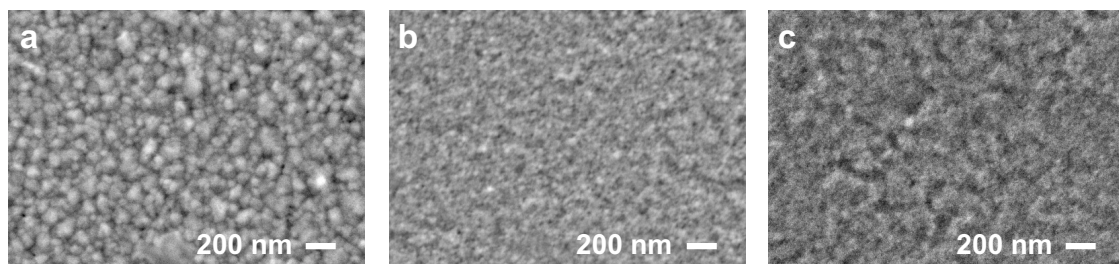


Figure S2. SEM images of (a) the 3D perovskite film, (b) the perovskite film with 0.04 M DPDA cation, and (c) the perovskite film with 0.04 M PDA cation.

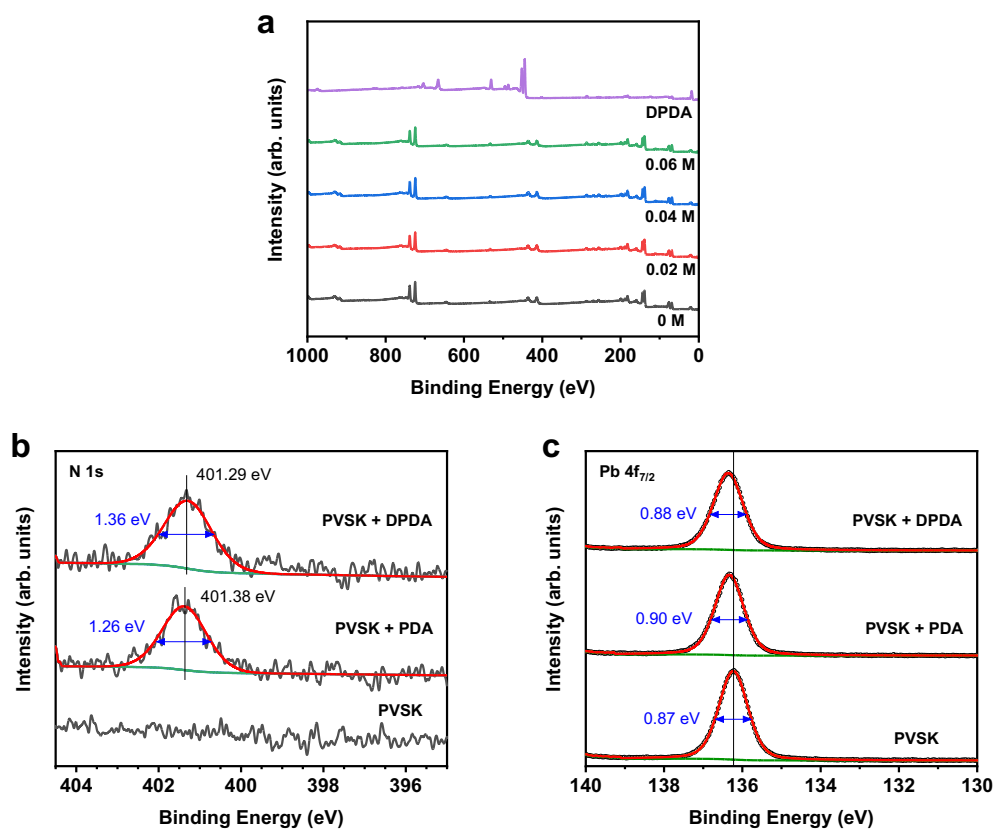


Figure S3. (a) XPS survey spectra of the pure-DPDA film and perovskite films with different DPDA ratios; XPS spectra of (b) N $1s$ and (c) Pb $4f_{7/2}$ core level regions of the CsPb(Br/Cl)₃ perovskite (PVSK) films with DPDA (0.04 M) and PDA (0.04 M) organic cations. The red and green curves correspond to XPS curve fittings and the Shirley background fittings, respectively.

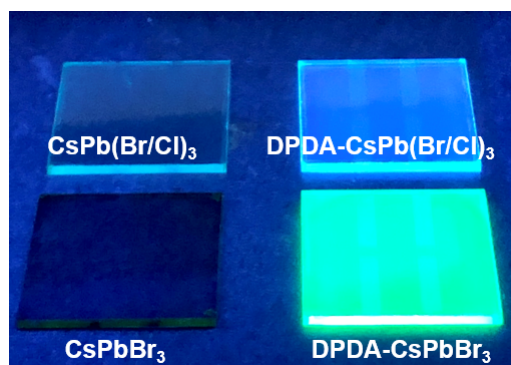


Figure S4. Photographs of the pure Br and mixed Br/Cl perovskite films without or with DPDA (0.04 M) excited under 365 nm ultraviolet radiation.

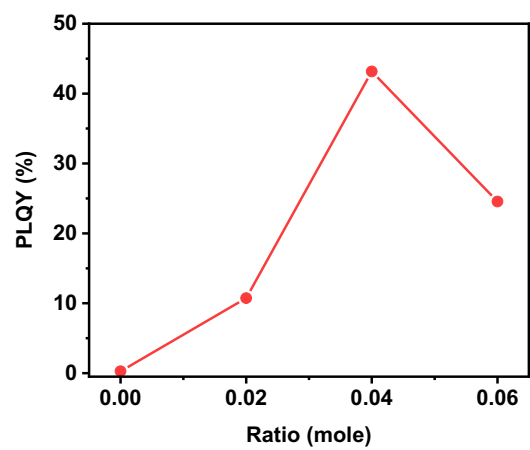


Figure S5. PLQY of the perovskite films with different DPDA ratios.

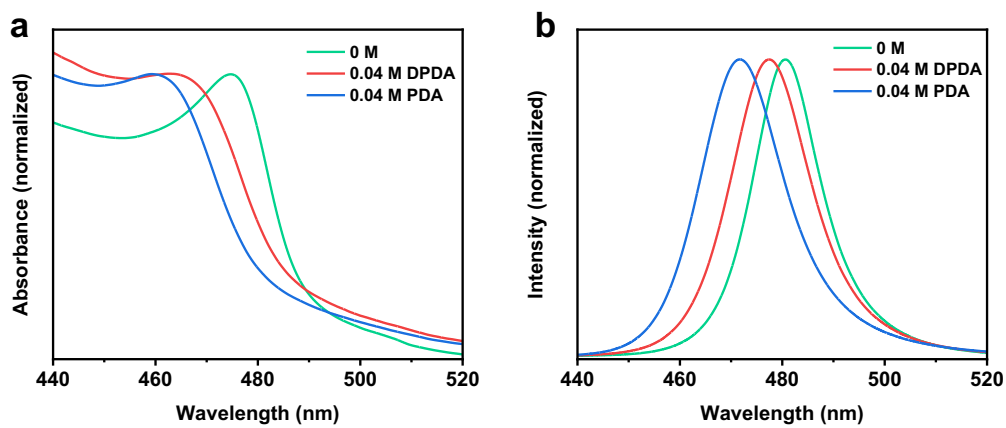


Figure S6. (a) Absorption spectra of the perovskite films; (b) Steady-state PL spectra of the perovskite films.

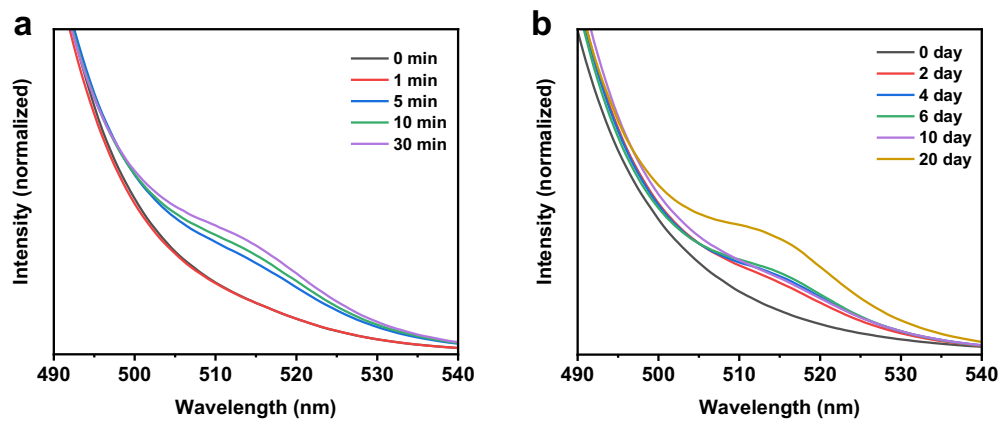


Figure S7. Steady-state PL spectra of the perovskite films (a) under irradiation within 30 min and (b) stored in air within 20 days.

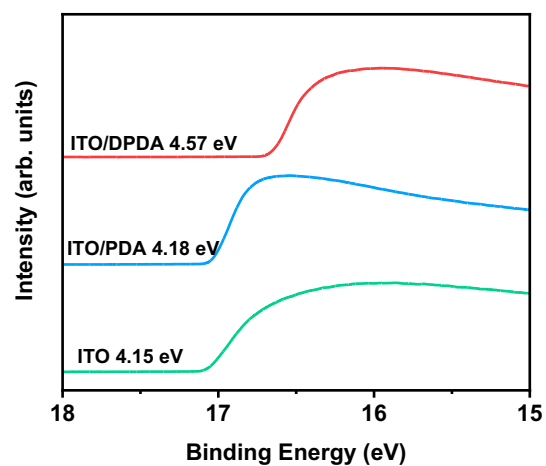


Figure S8. UPS spectra and the work function values of the bare ITO substrate, the ITO substrate with the PDA film, and the ITO substrate with the DPDA film.

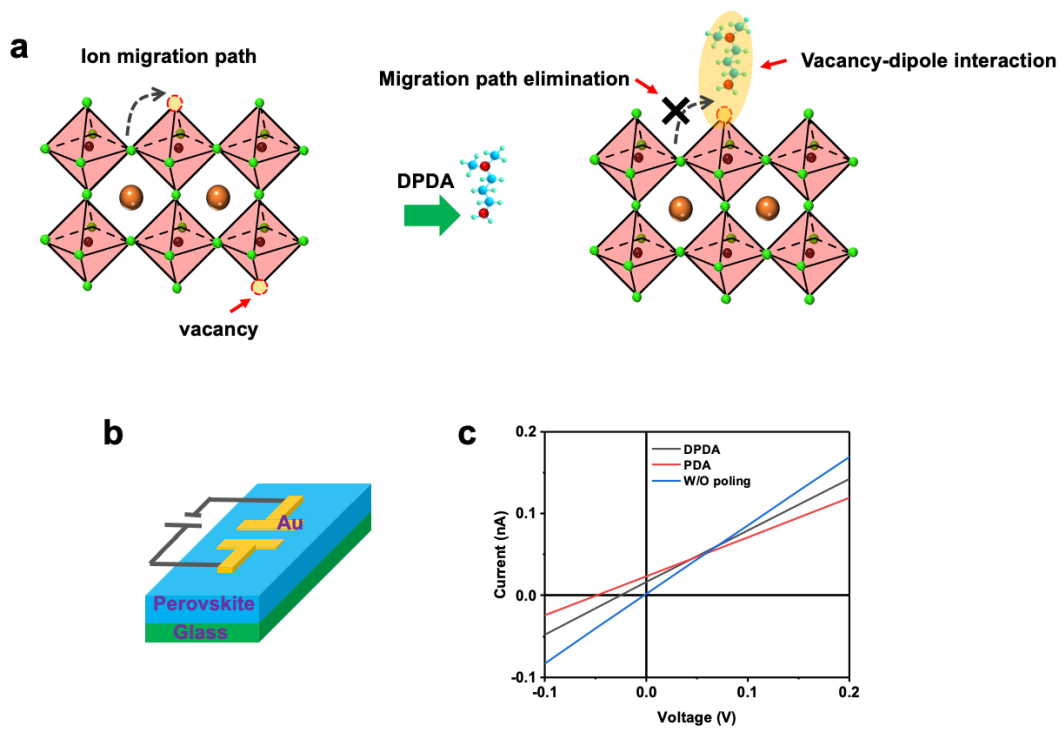


Figure S9. (a) Schematic drawing of ion migration path elimination by the vacancy-dipole interaction; (b) Schematic drawing showing the device structure for the electrical poling experiments on the perovskite films; (c) Current-voltage characteristics of the perovskite films after poling at 1 V for 1 min under light illumination of $\sim 10 \text{ mW/cm}^2$.

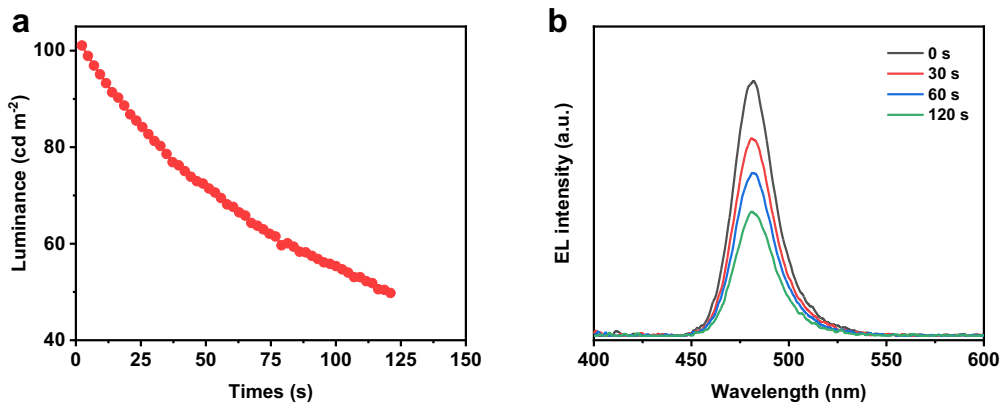


Figure S10. (a) Operational lifetime of the PeLED devices with an initial luminance of 100 cd/m²; (b) EL spectra of the PeLED device with DPDA-perovskites as the emitter layer.