Supporting Information

A Deep-dyeing Strategy for Ultra-stable, Brightly Luminescent Perovskite-polymer Composites

Caicai Zhang,‡[a,b] Ziqian He,‡[c] Mirra Mogensen,[d] Andre J. Gesquiere,[c,d] Chia-Hsun Chen,[e] Tien-Lung Chiu,[f] Jiun-Haw Lee,[g] Shin-Tson Wu,[c] and Yajie Dong*[a,b,c]*

[a] NanoScience Technology Center, University of Central Florida, Orlando, Florida, 32826, USA

[b] Department of Materials Science & Engineering, University of Central Florida, Orlando, Florida 32816, USA

[c] College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816, USA

[d] Department of Chemistry, University of Central Florida, Orlando, Florida 32816, USA

[e] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

[f] Department of Electrical Engineering, Yuan Ze University, Taoyuan 32003, Taiwan

[g] Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, Taipei 10617, Taiwan

Experimental Section

Materials: Commercial PET sheets with thickness of 80 μm and 30 μm were purchased from McMASTER-CARR. PET fibers with 20μm diameter were purchased from Goodfellow, 100 μm diameter PET fibers were purchased from Mono. Poly. CsCl (99.999%), $PbCl_2$ (99.999%), CsBr (99.999%), $PbBr_2$ (99.999%), CsI (99.999%), DMF (extra dry, 99%) and Dimethyl sulfoxide (DMSO) were all purchased from Sigma-Aldrich, while PbI_2 (99%) was purchased from ACROS Organics™ and MABr (99%) was purchased from Lumtec.

Preparation of DDPPCs: Perovskite precursors, including: 1) CsX and PbX_2 with a molar ratio of 1:1 and an overall concentration of 0.04 mmol/ml, 2) MAX and PbX_2 with a molar ratio of 3:1 and an overall concentration of 0.1-0.5 mmol/ml (X= Br^-, I^-), were prepared in DMF solvent and stirred to be fully dissolved, while CsCl and $PbCl_2$ was prepared in DMSO solvent. Octylamine/Oleylamine was added into the $CsPbX_3$ perovskite precursor solution with a concentration of 2-4 μl/ml. In $MAPbBr_3$ preparation, octylamine with a concentration of 2 μl/ml and oleic acid with a concentration of 1.2 μl/ml was used for preparing 0.5 mmol/ml $MAPbBr_3$. Other concentrations were prepared by dilution. The commercial PET sheets and fibers were immersed into the prepared precursor solutions inside of 20 ml solvothermal autoclaves. Close the autoclaves properly, and heated up the autoclave to 160℃ in an oven for 50 mins-1h, then cooled the autoclave to room temperature. For scaling-up DDPPCs, the commercial PET sheets were immersed into the 200ml solvothermal autoclaves and the autoclave were heated up to 160℃ in an oven for 2h 50 mins-3h accordingly, and then cooled to room temperature. Thereafter, the swelled PET sheets and fibers were immersed into 50-90℃ antisolvents for 1-15 mins, and baked at 80℃ on a hot plate for 2-6 hours to be fully deswelled. The final DDPPCs were obtained.

Characterization: The optical fluorescence images were taken from an Olympus BX51 microscope, where the excitation light source has a wavelength range of 450-480 nm. Spectra of DDPPCs were captured by Ocean Optics Spectrometer USB 2000+. TEM characterization analysis was carried out with JEOL TEM-1011. XRD patterns were performed on a PANalytical Empyrean X-ray diffractometer at 45 kV and 40 mA using Cu Kα radiation ($\lambda = 1.5406\mathring{A}$). The setup of PLQY measurement consisted of a light source, integrating sphere (Quanta-φ manual Rev C F-3029), monochromator (Horiba, iHR320) and photomultiplier tube (PMT). A single lamp housing (FL-1039A) with monochromator (180F) served as light source which can provide different excitation wavelength, 390 nm, 450 nm and 532 nm for blue, green and red emission in this research, respectively. After excited the samples in integrating sphere, fluorescence can be collected by monochromator and PMT through optical fiber. Then PLQY values can be obtained by measure the difference between blank substrate and samples with software calculations (FluorEssence). With a home-built sample-scanning confocal microscope described elsewhere[58], Time correlated single photon counting (TCSPC) excited state lifetime studies were completed by parking an area of interest of the samples over the focused pulsed laser beam (Picoquant LDH-P-C-470), and collecting photons with a fast single photon counting detector (Picoquant, Micro Photon Devices, PDM series). Photon timing was measured using a PDL 800-D pulsed laser driver that provided the timing signal to a PicoHarp 300 TCSPC module in combination with a PHR 800 detector router, all from Picoquant.

Stability tests: The water stability test was prepared by directly putting the DDPPCs into the deionized mater at room temperature for over two years.

For the thermal stability tests, the samples were put inside the Linkam LTS350 Cryostat. Laser excitation at 457 nm (Cobolt Twist™) was applied towards the DDPPC films, which is heated up on the stage with a rate of 5 ℃/min. The temperature was controlled by Linkam TMS 94 which is a precise temperature controller. During the thermal stability test, the DDPPCs will

be heated up to the set temperature, and keep the temperature stable for 2 to 3 minutes, and then measure the PL spectra accordingly, then heading to the next temperature points.

For the damp-heat tests, the samples were stored in a home-made incubator with 70 °C and 90% RH under normal room lighting, while the references were stored in dark ambient air at room temperature. When conducting relative PL measurements, the samples were taken out from the incubator and cooled down to room temperature. A 457-nm blue laser (Cobolt Twist™) with an irradiance of 10 mW/cm^2 was applied as the excitation light source and the PL spectra of both references and samples were recorded by a spectrometer (Ocean Optics Spectrometer USB 2000+). All the stability tests were carried out on as-prepared bare films without any additional barrier protection.

To measure the photo-stability, the samples were mounted on a fixed stage. A 457-nm blue laser (Cobolt Twist™) with a continuous irradiance of 100 mW/cm^2 was applied as the excitation light source. The PL emission spectra were in-situ recorded by a optical spectrometer (Ocean Optics Spectrometer USB 2000+).

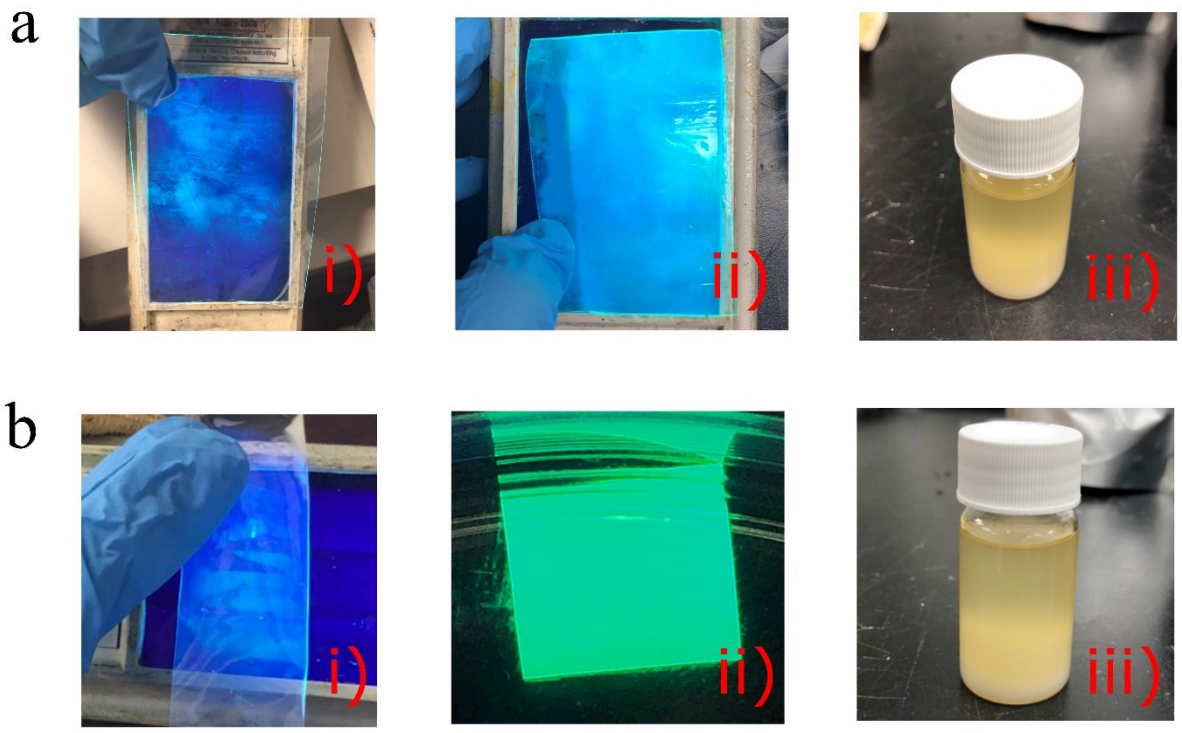

Figure S1. a) Deep-dyed $MAPbBr_3$-PET films under different swelling temperature for 1h: i) 130 ℃, ii) 160 ℃, iii) 190 ℃. As a result, i) with 130 ℃, the film is not fully swelled; ii) with 160 ℃, the film is sufficiently swelled; iii) with 190 ℃, the film is dissolved. b) Deep-dyed $MAPbBr_3$-PET films under different swelling time at 160 ℃: i)0.5 hr, ii) 1 hr, iii) 1.5 hr. As a result, i) with 0.5 hr, the film is not fully swelled; ii) with 1 hr, the film is sufficiently swelled; iii) with 1.5 hr, the film is dissolved.

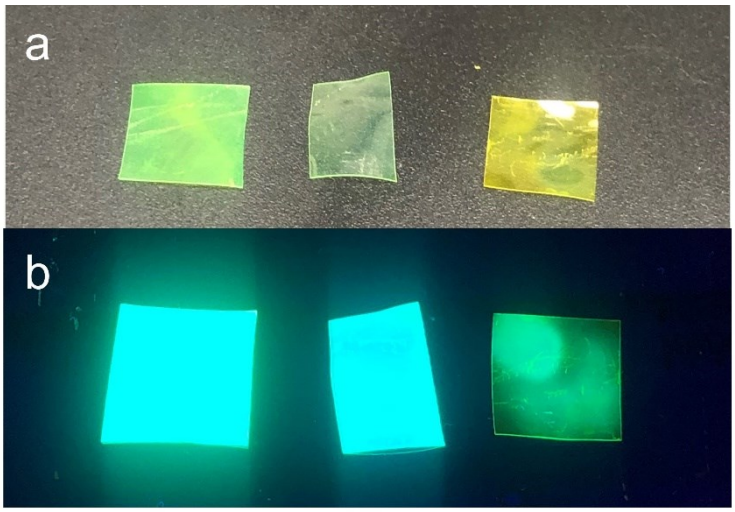

Figure S2. Deep-dyed PET films under different deswelling conditions. a) Films under ambient light. b) Films under UV excitation. From left to right: 1) antisolvent treated at 85 ℃ for 1 min; 2) blow-dried at 145 ℃ for 5 min; 3) blow-dried at 260 ℃ for 1 min.

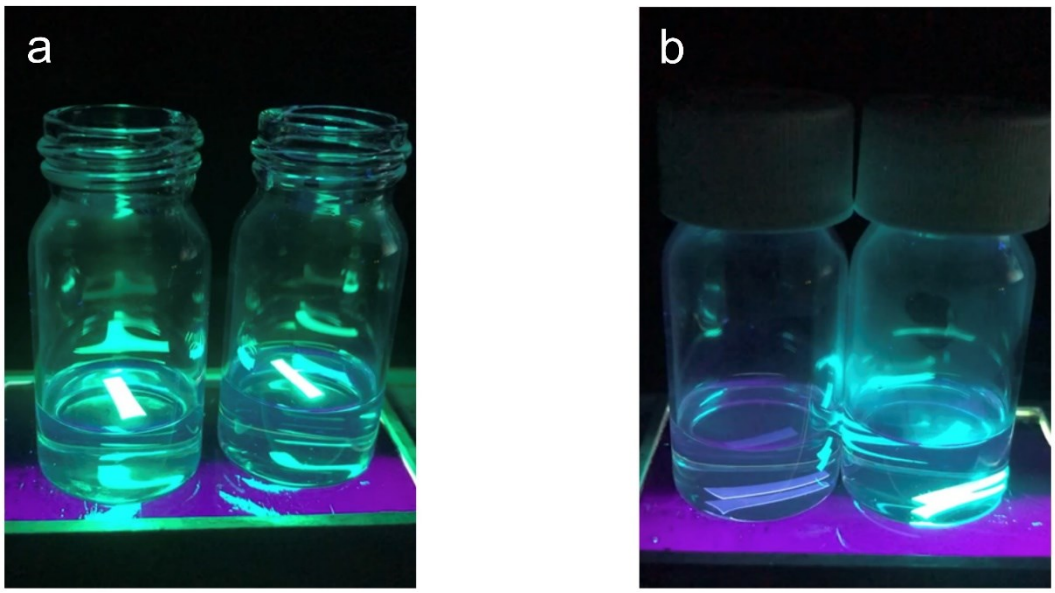

Figure S3. a) $MAPbBr_3$-PET DDPPC films prepared without baking (left) and with baking (right) treatment immersed in DMF solvent for 0 min. b) $MAPbBr_3$-PET DDPPC films prepared without baking (left) and with baking (right) treatment immersed DMF solvent for 2 min.

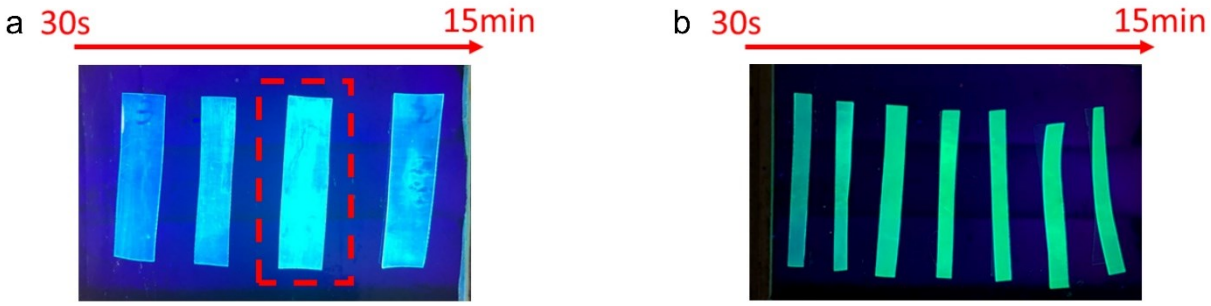

Figure S4. Antisolvent comparison in the deswelling step of the DDPPCs: a) 50 ℃ isopropyl alcohol as the antisolvent; b) 85~90 ℃ toluene as the antisolvent.

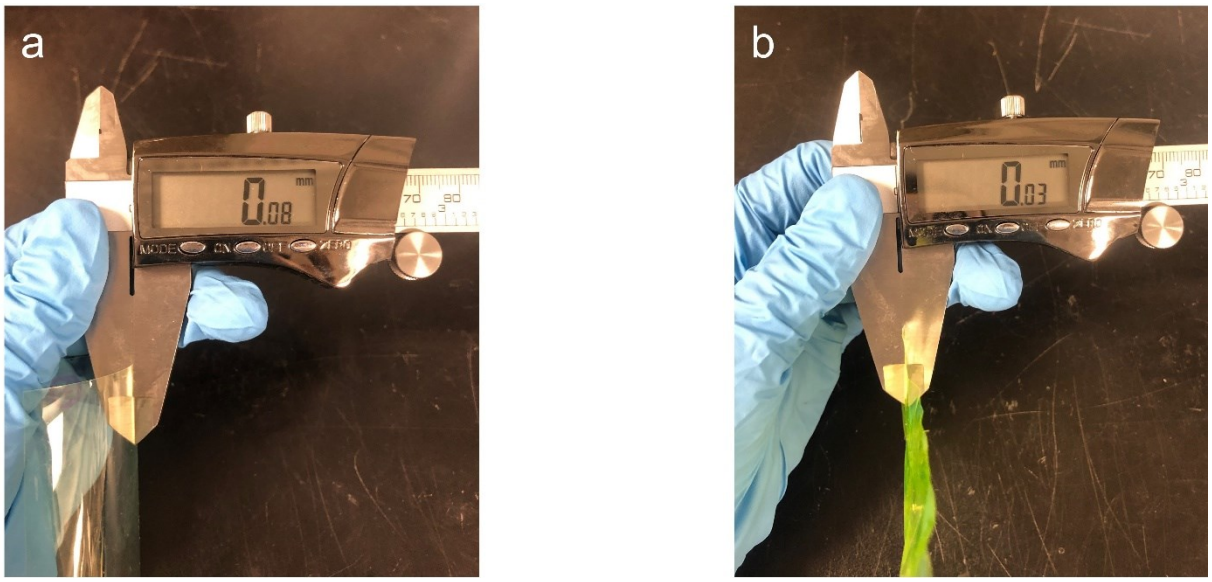

Figure S5. DDPPC films with different film thickness: a) 80 µm; b) 30 µm.

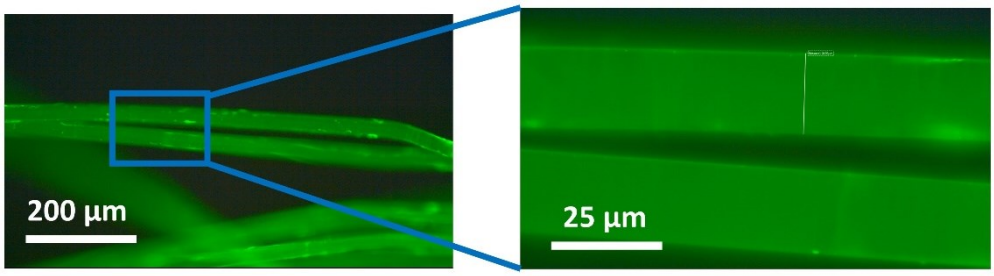

Figure S6. Fluorescence optical microscope images of $MAPbBr_3$-PET DDPPC fibers. Fiber diameter: 20 µm.

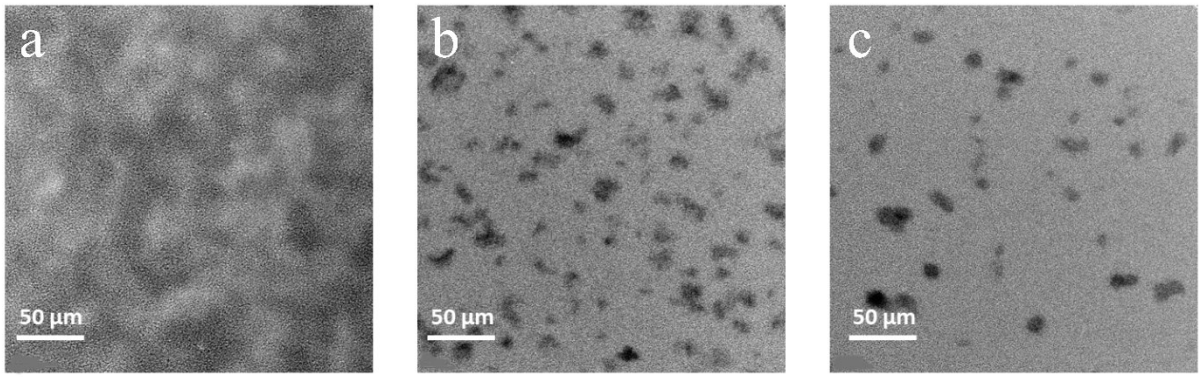

Figure S7. Cross-section TEM images of a) a blank PET film, b) an $MAPbBr_3$-PET DDPPC film, and c) a $CsPbBr_{0.75}I_{2.25}$-PET DDPPC film.

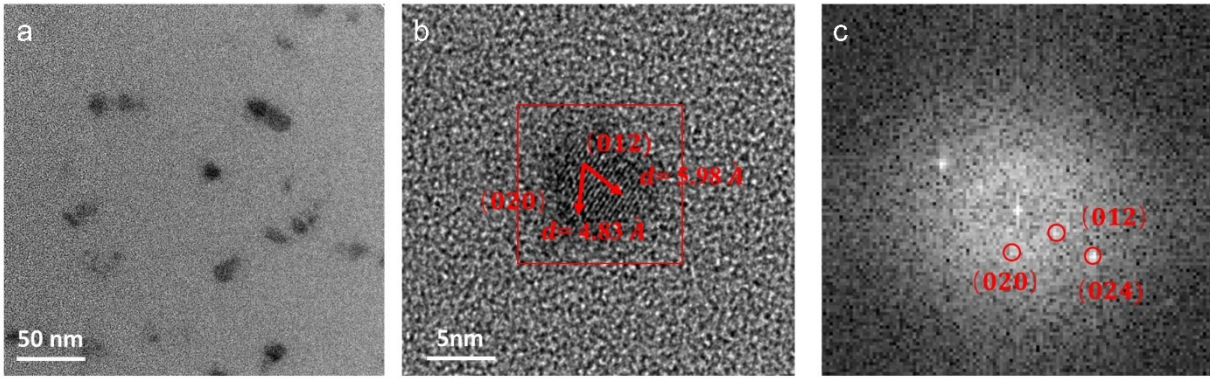

Figure S8. a) Cross-section TEM image of $CsPbBr_{0.75}I_{2.25}$-PET DDPPC film. b) HRTEM image of $CsPbBr_{0.75}I_{2.25}$ nanocrystals showed in a). c) FFT of b).

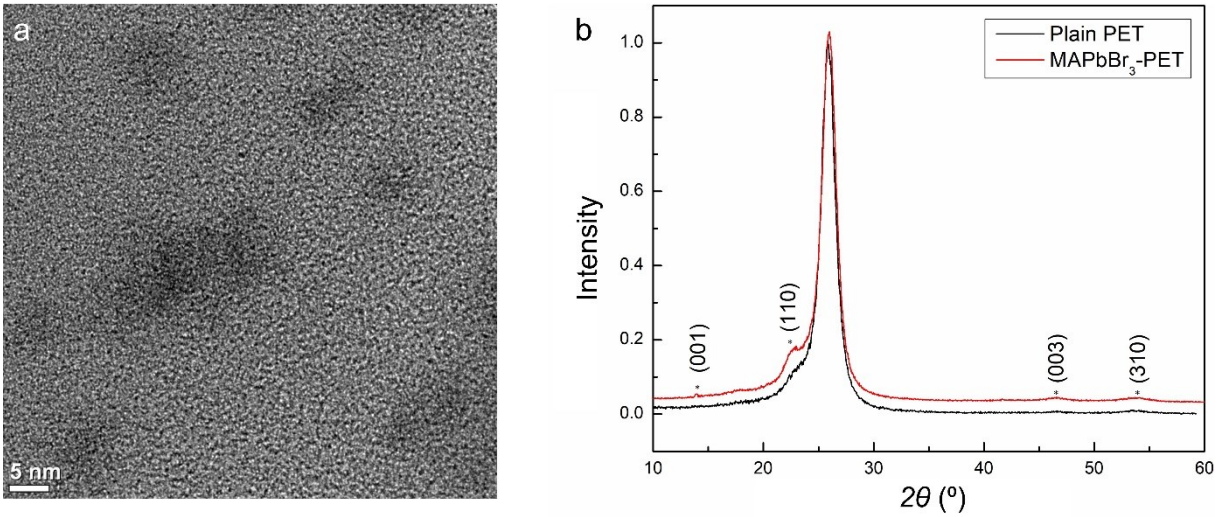

Figure S9. a) HRTEM image of $MAPbBr_3$-PET DDPPC film. b) XRD characterization of $MAPbBr_3$-PET DDPPC film.

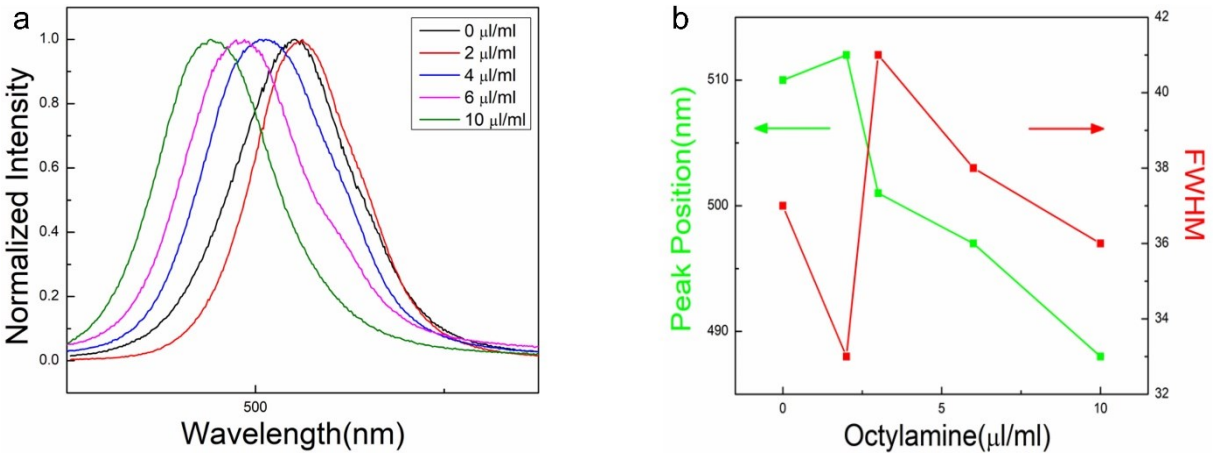

Figure S10. a) Photoluminescence emission spectra of $MAPbBr_3$-PET DDPPC films with different octylamine amount. b) The peak position and FWHM change with different octylamine amount.

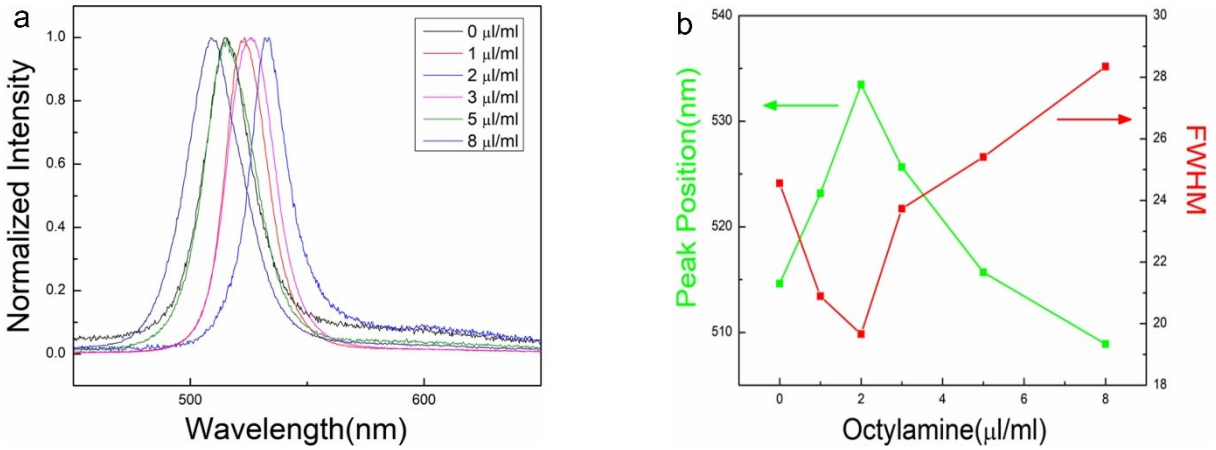

Figure S11. a) Photoluminescence emission spectra of $CsPbBr_3$-PET DDPPC films with different octylamine amount. b) The peak position and FWHM change with different octylamine amount.

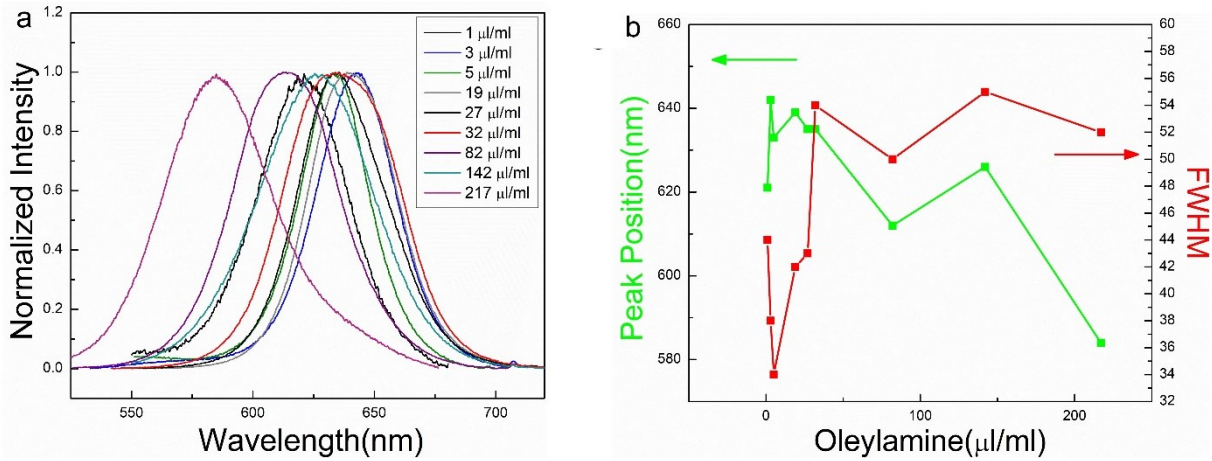

Figure S12. a) Photoluminescence emission spectra of $CsPbBr_{0.75}I_{2.25}$-PET DDPPC films with different octylamine amount. b) The peak position and FWHM change with different octylamine amount.

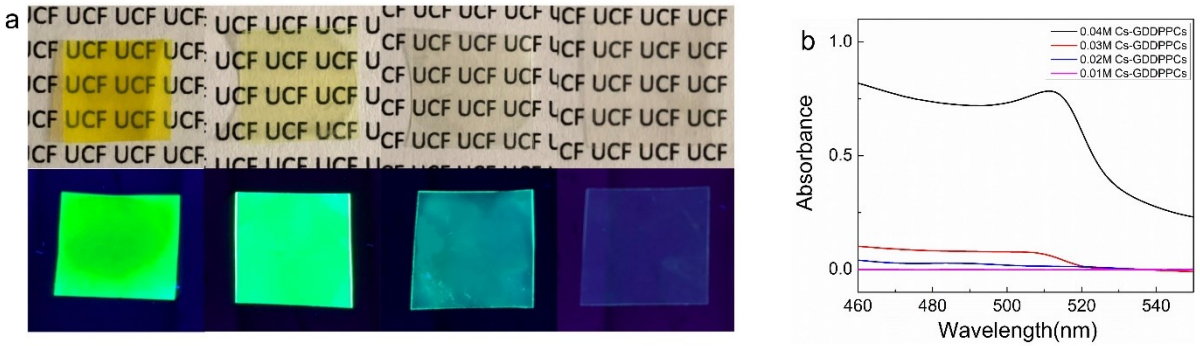

Figure S13. Optical density control of DDPPC films.

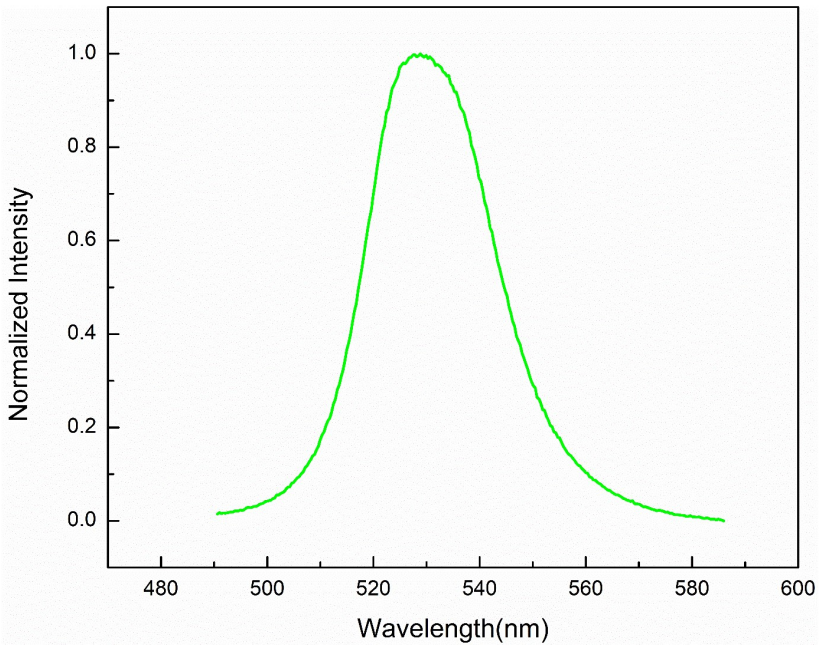

Figure S14. Photoluminescence emission spectra of $MAPbBr_3$-PET DDPPC fiber.

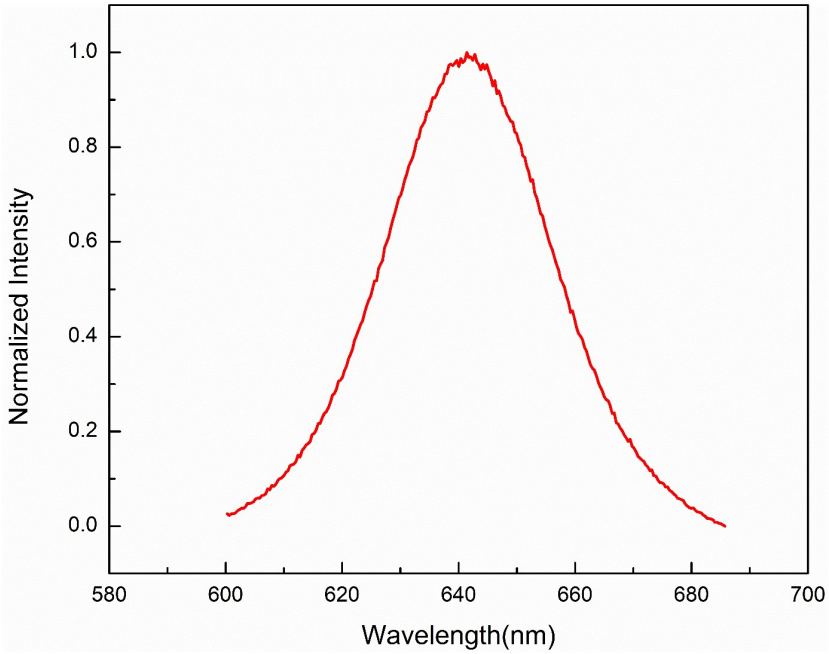

Figure S15. Photoluminescence emission spectra of $CsPbBr_{0.75}I_{2.25}$-PET DDPPC fiber.

Table S1: The fitting parameters of PL decay curves for various DDPPCs.

Materials	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_3 (ns)	f_3 (%)	τ_4 (ns)	f_4 (%)	$\tau_{avg.}$ (ns)
$MAPbBr_3$	2330	84.78	304	7.56	32.6	4.18	7.79	3.48	2000
$CsPbCl_1Br_2$	136	14.93	18.98	20.73	0.998	24.26	4.058	40.08	26
$CsPbBr_3$	464	26.65	103	35.46	23.54	29.26	4.52	8.63	167
$CsPbBr_{0.75}I_{2.25}$	288	17.64	64.77	31.64	6.55	7.27	19.46	43.46	80

The time resolved photoluminescence lifetime were fitted with a quadruple-exponential function:

$F(t) = f_1 \cdot e^{-t/\tau_1} + f_2 \cdot e^{-t/\tau_2} + f_3 \cdot e^{-t/\tau_3} + f_4 \cdot e^{-t/\tau_4}$

where f_i is the relative ratio factor, τ_i is the time constant.

The average recombination lifetime $\tau_{avg.}$ is estimated with the f and τ values from the fitted curve data according to the following equation:

$\tau_{average} = f_1\tau_1 + f_2\tau_2 + f_3\tau_3 + f_4\tau_4$

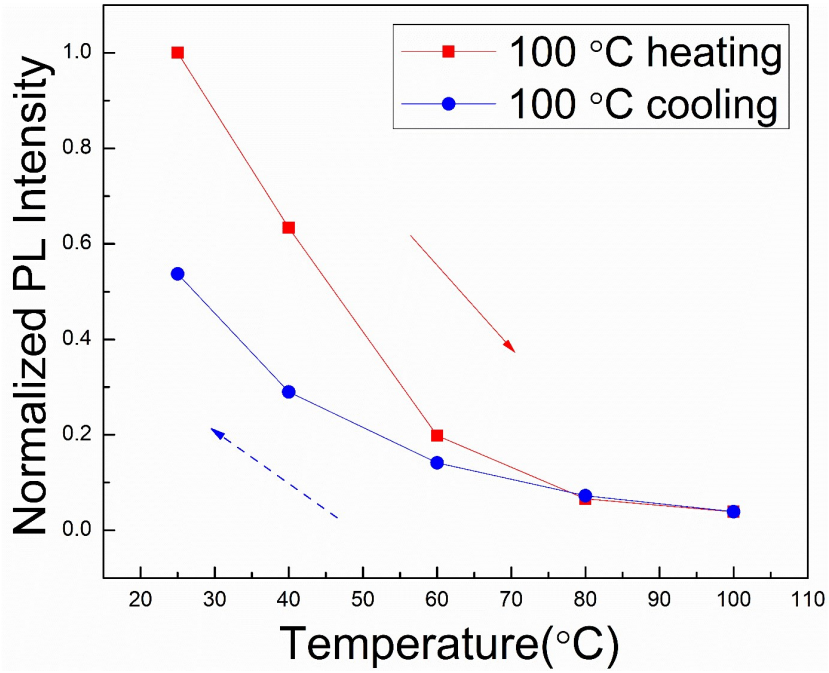

Figure S16. Temperature dependent PL intensity of $CsPbBr_3$-PET DDPPCs during a 100 ℃ heating-cooling cycle.

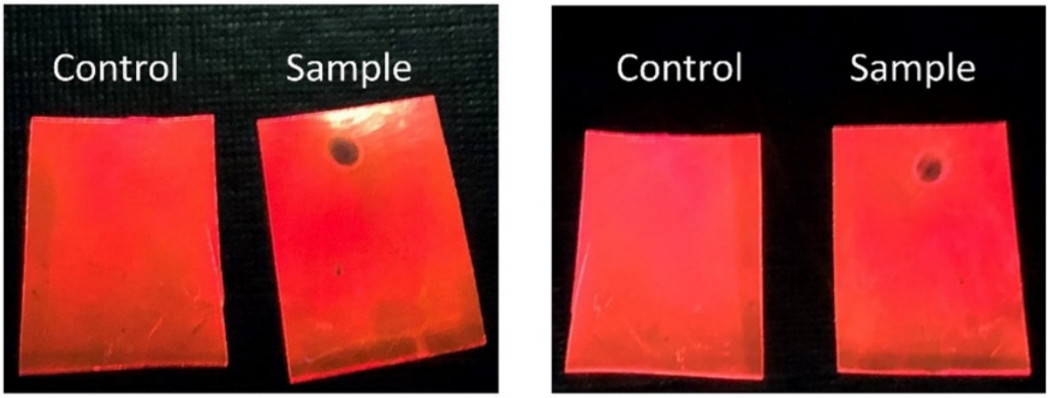

Figure S17. Visual comparison of PL intensity between $CsPbBr_{0.75}I_{2.25}$-PET DDPPC sample and control in the damp-heat test a) on first day and b) after 60 days.

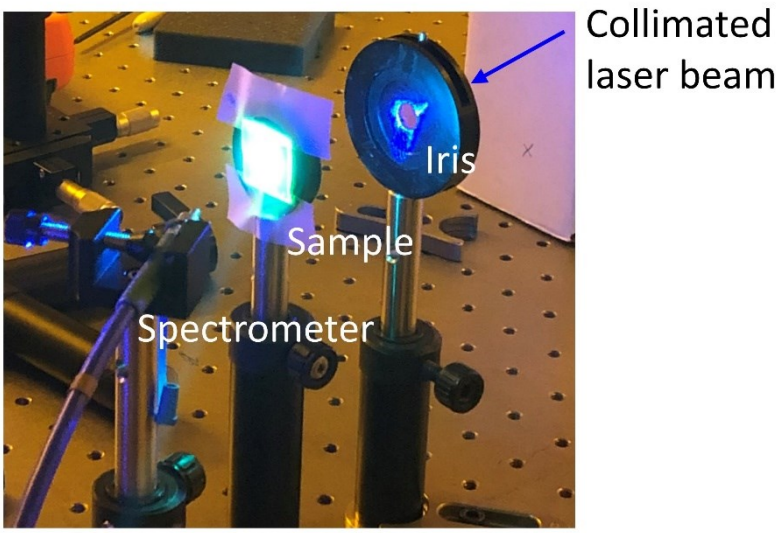

Figure S18. Optical setup of the in-situ photo stability test of DDPPC films.

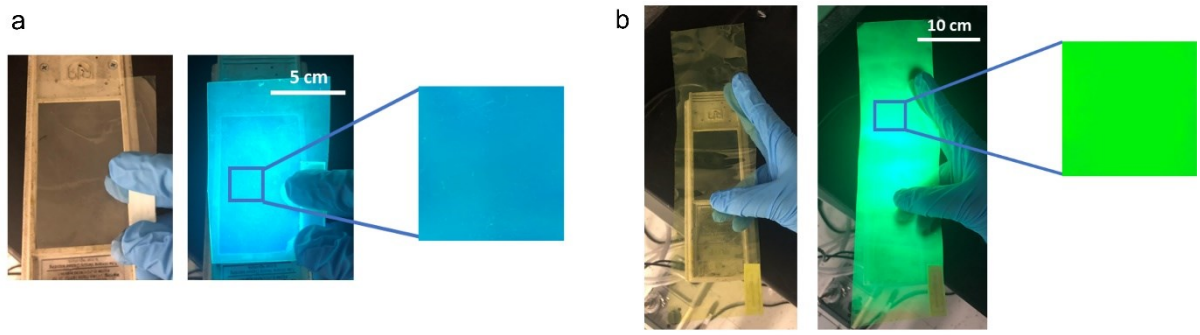

Figure S19. a) $MAPbBr_3$-PET and b) $CsPbBr_3$-PET DDPPC films with scaled up. From left to right: scaled up films under ambient light; scaled up films with UV excitation; zoom-in view of the scaled-up films.