Supporting Information

Efficient Near-Infrared Light-Emitting Diodes Based on Organometallic Halide Perovskite-Poly(2-ethyl-2-oxazoline) Nanocomposite Thin Films

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Experimental

Film and device fabrication: ITO-coated glass substrates were cleaned successively with detergent, acetone and ethanol, followed by drying and 15 min UV-ozone treatment. PEDOT:PSS (Celvios P VP AI 4083) was spin-coated onto the ITO substrate at 3000 r.p.m. for 40 s, and annealed at 120 °C for 20 min in air. The nanocomposite films were obtained from poly(2-ethyl-2-oxazoline) (PEtOz), methylammonium iodide (MAI) and lead iodide (PbI$_2$) blend solution in a binary solvent mixture of γ-butyrolactone and dimethyl sulfoxide with a volume ratio of 7:3. The molar ratio of MAI: PbI$_2$ was fixed at 1:1 while varying the PEtOz weight ratios in the powder blend. The total weight ratio of the blend precursor solution was kept at 35 wt%. Both pristine and perovskite-PEtOz films were spin-coated at 5000 r.p.m. for 40 s, and the substrate was treated with 140 uL toluene drop-casting during spin-coating process. After thermal annealing and crystallization of the perovskite at 100 °C for 10 min,

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PC$_{60}$BM was spin-coated onto the perovskite layer at 3000 r.p.m. for 40 s. Ag cathode was subsequently deposited by vacuum thermal evaporation under high vacuum and defined the active area of 0.06 cm^2 for our NIR PeLED devices.

Characterization: The current-voltage-radiance characteristics were measured in air using a Keithley 2635 source measurement unit in conjunction with a Newport 818-UV Silicon photodiode centred over the light-emitting pixel. Absorption, steady-state PL, and EL spectra were measured with an Ocean Optics QE-Pro spectrometer. Time-resolved PL spectroscopy was conducted with an Edinburgh Instruments FLS920 fluorescence spectrometer. The work functions were measured by a KP Technology SKP5050 Scanning Kelvin Probe System with a resolution of 1-3 meV.
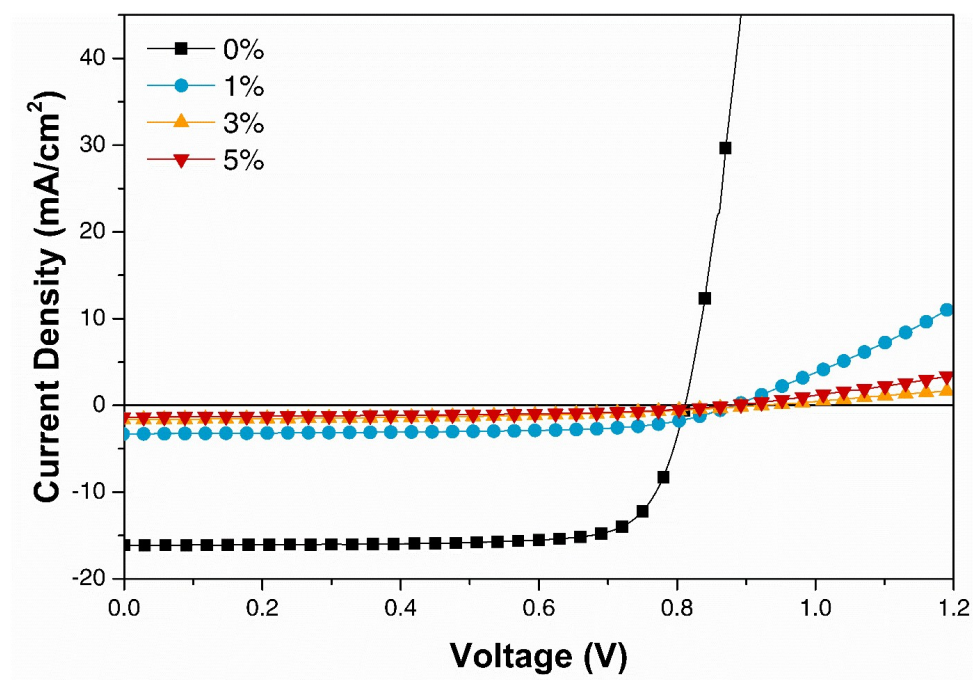
Solar cell performance

Figure S1. J-V characteristics of solar cell devices using the PEtOz-nanocomposite thin films as active layers.

Morphology characteristics

AFM characteristics of nanocomposite films with 0% - 8% PEtOz content
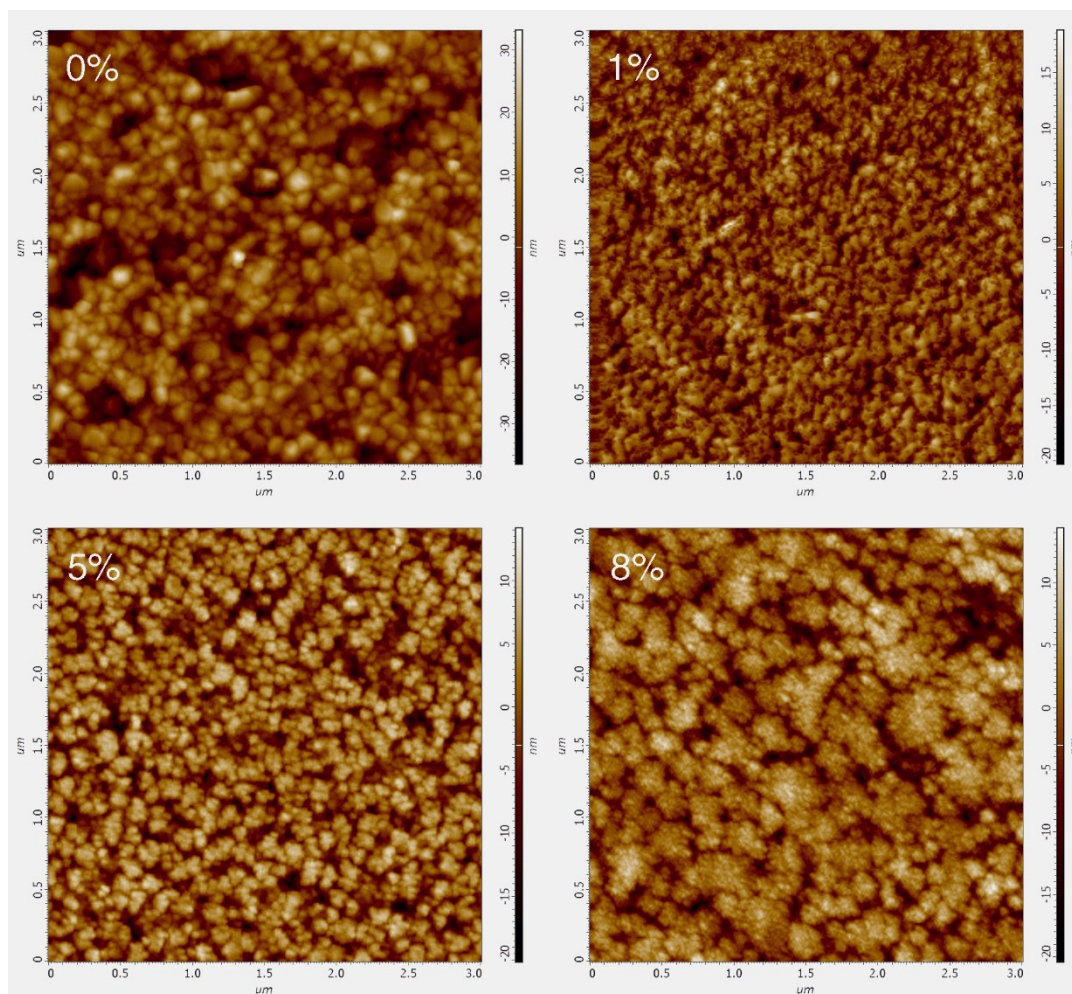

Figure S2. AFM images of perovskite-PEtOz nanocomposite films on glass/PEDOT:PSS substrates. The RMS roughness is 8.7, 4.7, 5.1 and 4.8 nm for the films with 0%, 1% 5% and 8% PEtOz content, respectively.
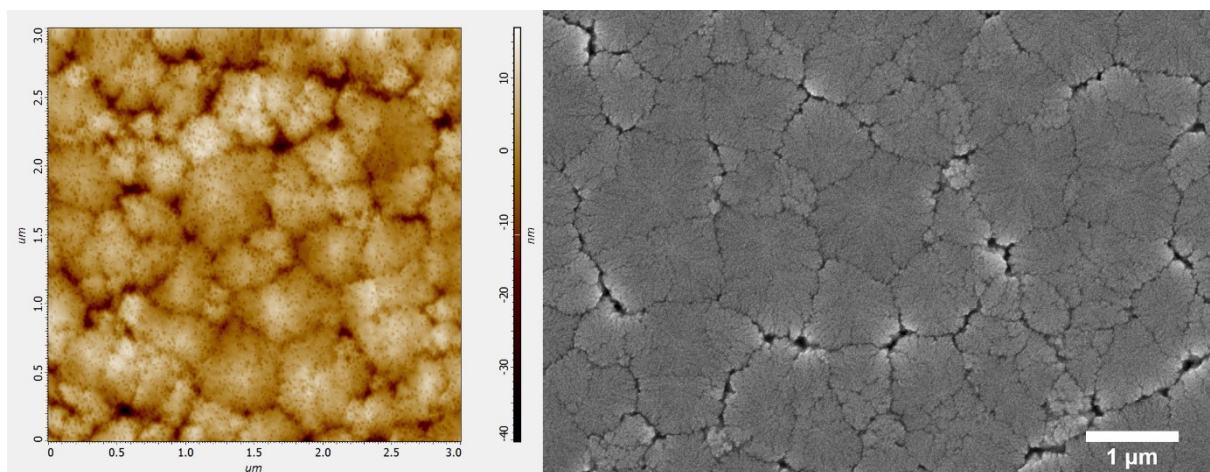
Figure S3. AFM and SEM images of the perovskite-PEtOz film with 15% PEtOz content, showing that the excess of PEtOz precipitates and forms micrometer-sized particles at the surface of the perovskite layer.
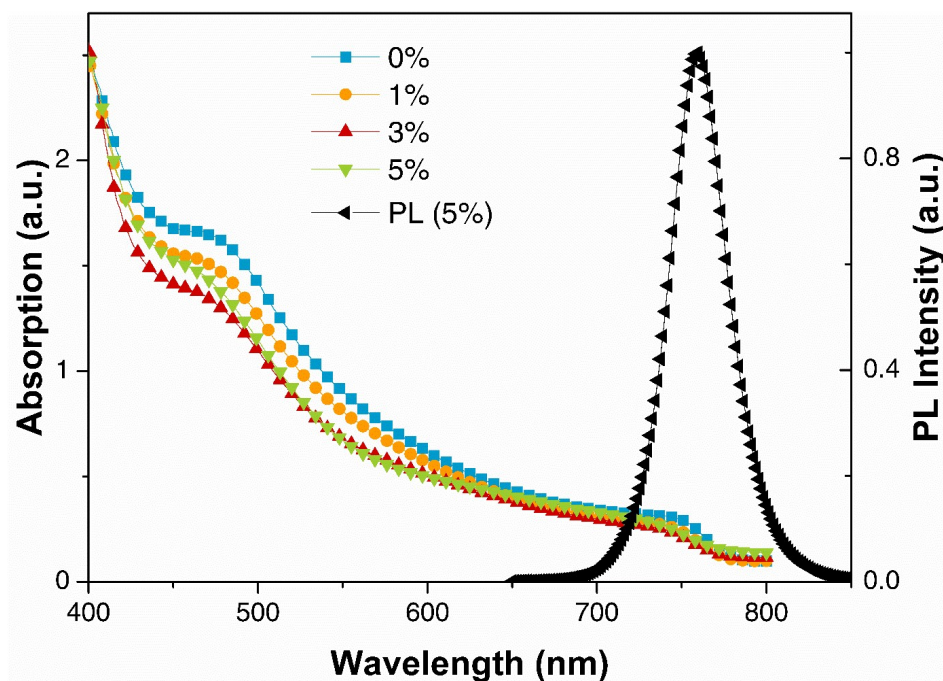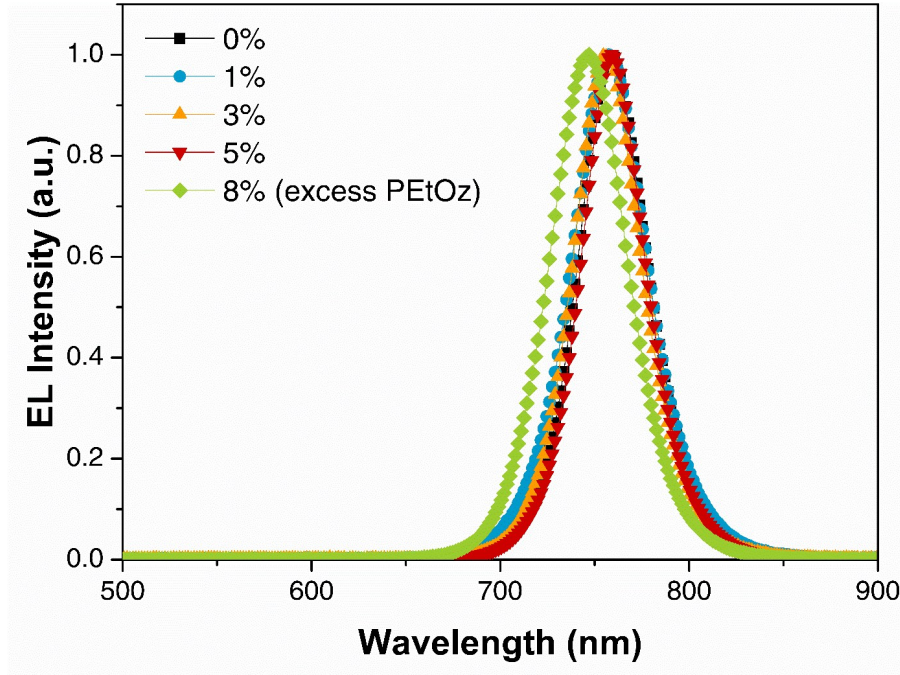
Spectra characteristics

Figure S4. UV-vis absorption spectra of perovskite-PEtOz thin films with different PEtOz content; PL spectrum of the perovskite film with 5% PEtOz content is also presented.

Figure S5. EL spectra of PeLEDs with different PEtOz weight ratios. The small variation in the spectrum profile from 0% to 5% devices can be attributed to the light scattering caused by the PEtOz polymer matrix. The blueshift observed in the 8% device is caused by quantum confinement of excitons with smaller nanocrystals formed at higher PEtOz concentrations.

Time-resolved photoluminescence analysis

Time-resolved photoluminescence spectroscopy (TR-PL) was used to study the recombination lifetimes of the perovskite samples. The PL decay curves were registered at λ_{em} of 760 nm with excitation from a 405 nm pulsed laser and fitted using a multi-exponential function:

$$I(t) = \sum_{i=1}^{n} B_i \exp(-t/\tau_i), \quad \tau_i > 0 \qquad \backslash^* \text{ MERGEFORMAT (S1)}$$

where τ_i represent the decay time constants, B_i represents the normalized amplitudes of each component and n is the number of decay times. In this paper, we used a tri-exponential mode (n=3), and the amplitude weighted average decay lifetime τ_{avg} of the PL decay process can be calculated from:

$$\tau_{avg} = \frac{\sum B_i \tau_i^2}{\sum B_i \tau_i} \qquad \qquad \text{\textbackslash* MERGEFORMAT (S2)}$$

Table S1 summarizes the lifetimes obtained from the TR-PL measurements. In which, f_i is the fraction of fluorescence intensity in % that calculated from B and τ by:

$$f_i = \frac{B_i \cdot \tau_i}{\sum_{i=1}^{n} B_i \tau_i} \times 100\% \qquad \qquad \text{\textbackslashMERGEFORMAT}$$

(S3)

Table S1. PL lifetimes obtained from TR-PL of PEtOz-perovskite composite films.

PEtOz	f_1	τ_1 (ns)	f_2	τ_2 (ns)	f_3	τ_3 (ns)	χ^2	τ_{avg} (ns)
0%	44.332	0.882	40.263	3.704	15.405	16.917	1.208	4.5
1%	33.24	2.881	34.339	11.249	32.362	58.861	1.155	23.9
3%	30.855	6.344	42.294	31.541	26.851	168.845	1.116	61
5%	13.93	23.205	49.556	126.485	36.515	486.364	1.148	243

Charge-carrier Measurement for PEtOz-nanocomposite Thin Films

As illustrated in Figure S1, the open-circuit voltage increases as the PEtOz content increases, which implies a higher charge carrier density inside the active layer with PEtOz confinement. We have attempted to verify this charge confinement by measuring the charge-carrier mobility in our nanocomposite thin films. However, in the field-effect transistor configuration the lateral current obtained from the source-drain is even lower than the leakage current from source-gate and did not show any transistor characteristics. Also from the Hall effect measurements we cannot get the mobility in the lateral direction, but the charge-carrier density of the samples in the magnitude of 2×10^{14} cm^{-3} were obtained when 5 kG magnetic field was applied. Hence, a longitudinal metal-semiconductor-metal system (Au/perovskite-PEtOz/Au) was considered, using a simple function of $J = q\mu nE$ to estimate the charge-carrier mobility since the current is directly proportional to the field that obeys Ohm's law. (J is the measured current density, E is the applied electric field, q is the elementary charge, and n is the measured charge-density).

From Figure S6, the estimated charge-carrier mobility in films with 0% and 5% PEtOz are 0.7 cm^2 V^{-1} s^{-1} and 3.3×10^{-3} cm^2 V^{-1} s^{-1}, respectively. The reduced mobility in PEtOz-nanocomposite perovskite films confirms the formation of a PEtOz dielectric matrix that confines the charge carries inside the perovskite crystals. These mobility data were used to calculate the diffusion length in our perovskite-PEtOz thin films.
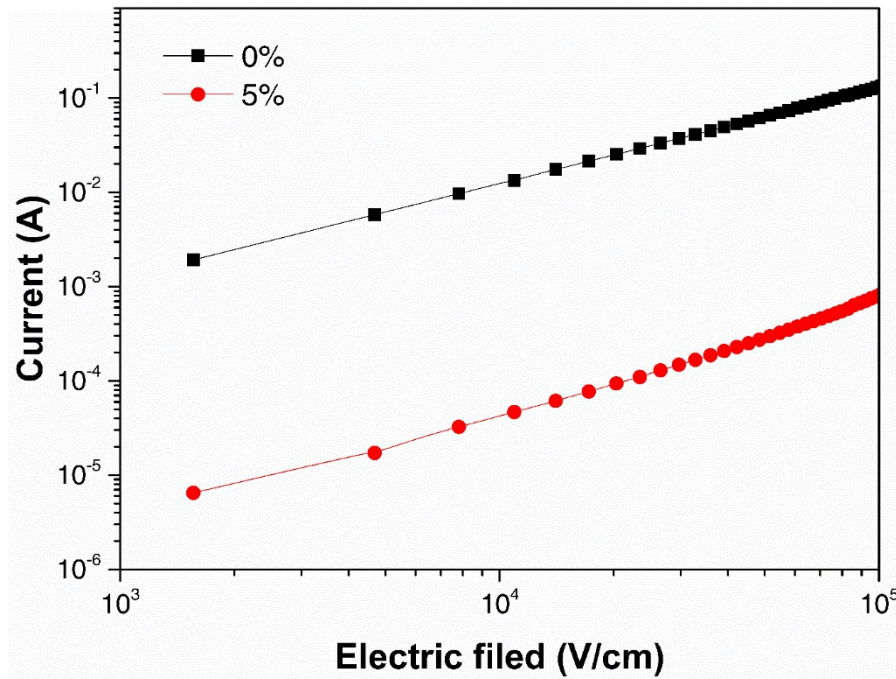

Figure S6. Electric filed versus current for metal-semiconductor-metal (Au /perovskite-PEtOz /Au) devices with 0% and 5% PEtOz content.