

Electronic Supplementary Information

Bright and Efficient Blue Polymer Light Emitting Diodes with Reduced Operating Voltages Processed Entirely at Low-Temperature

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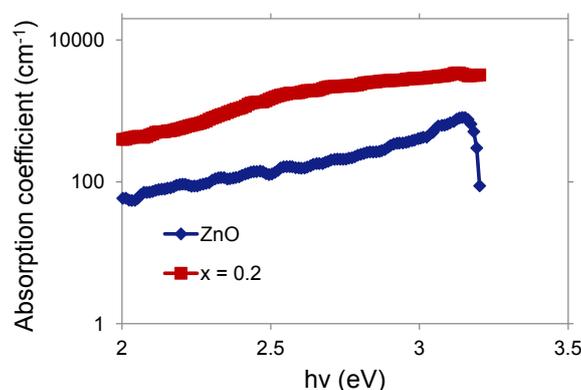


Fig. S1 Absorption measurements of the sub-bandgap states in AP-CVD $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ deposited at 150 °C. These measurements were obtained by photothermal deflection spectroscopy for our previous work on quantum dot solar cells in Ref. 1. To more clearly show the absorption due to sub-bandgap states, we have subtracted the contribution to the absorption by band-tail states and displayed the result here. These indicate that sub-bandgap states occur 1 eV below the band-edge at 3.3 eV, due to the non-zero absorption coefficient. More details on obtaining the band-tail absorption through fitting the band-edge with the Urbach model can be found in the Supporting Information of Ref. 1. Ref. 1 also shows the full absorption spectra without the Urbach tails removed.

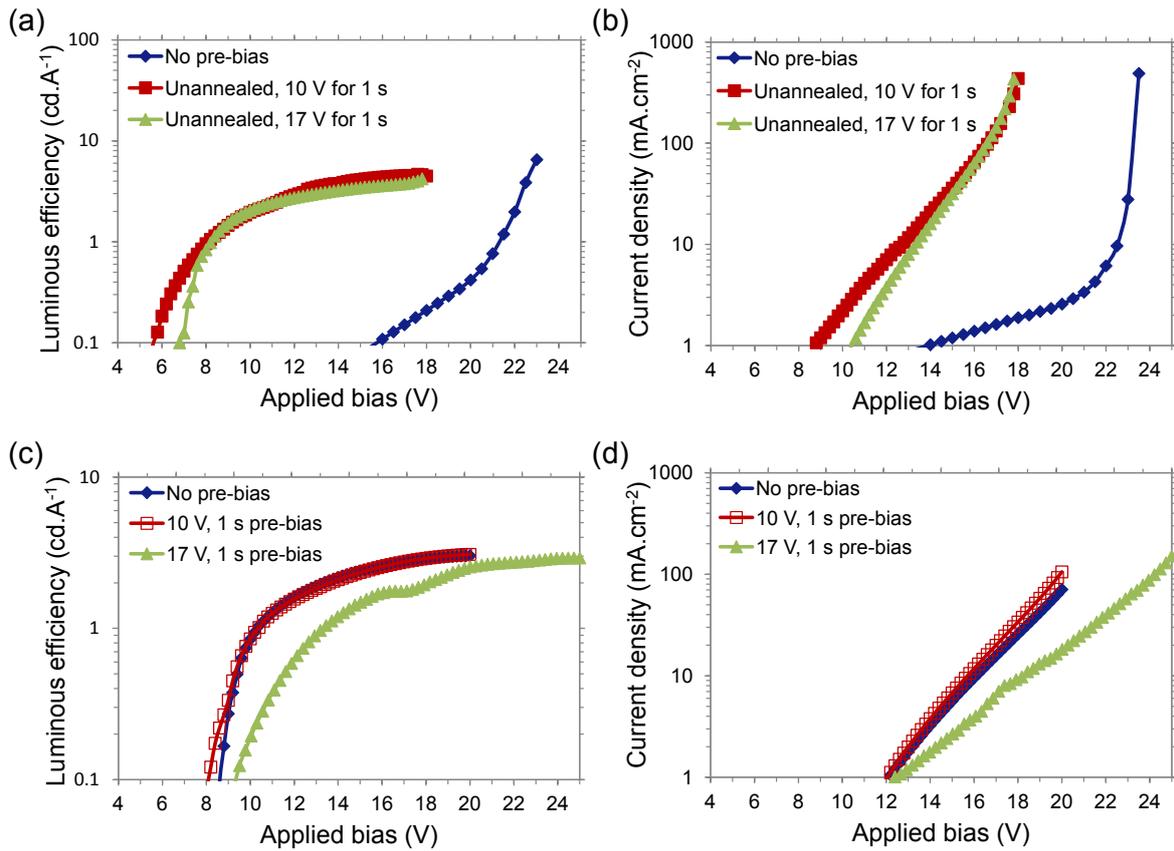


Fig. S2 Optimizing the pre-biasing voltage (no-prebias compared to pre-biasing the PLEDs at 10 V and 17 V for 1 s before measuring). (a) Luminous efficiency and (b) current density vs. applied bias of aryl-F8:0.5 wt.%TFB PLEDs with unannealed $Zn_{0.85}Mg_{0.15}O$. (c) Luminous efficiency and (d) current density vs. applied bias of the same PLEDs but using ZnO annealed at 400 °C for 15 min in air. These show that pre-biasing at 10 V for 1 s is optimal for reducing the operating voltage without degrading the device and the pre-biasing effect is larger in the PLEDs with unannealed oxides.

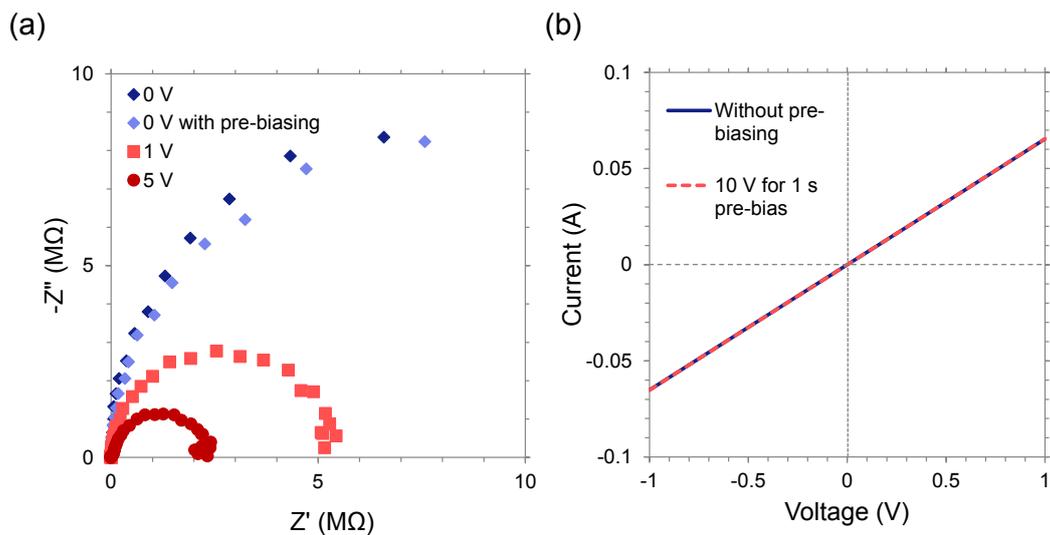


Fig. S3 (a) Nyquist plots for our bipolar blue PLEDs at different D.C. biases. These show only one semicircle after pre-biasing or with the application of a non-zero D.C. bias, which suggests no extra capacitance due to surface dipoles occurred.² A Solartron Impedance Analyzer was used with an A.C. amplitude of 10 mV. For the PLED analyzed, annealed ZnO/ $Zn_{0.85}Mg_{0.15}O$ was used. (b) Current – voltage plot of ITO/ZnO/Ca/Ag stack without and with pre-biasing at 10 V for 1 s. This shows that the conductivity of the oxide was unchanged after pre-biasing.

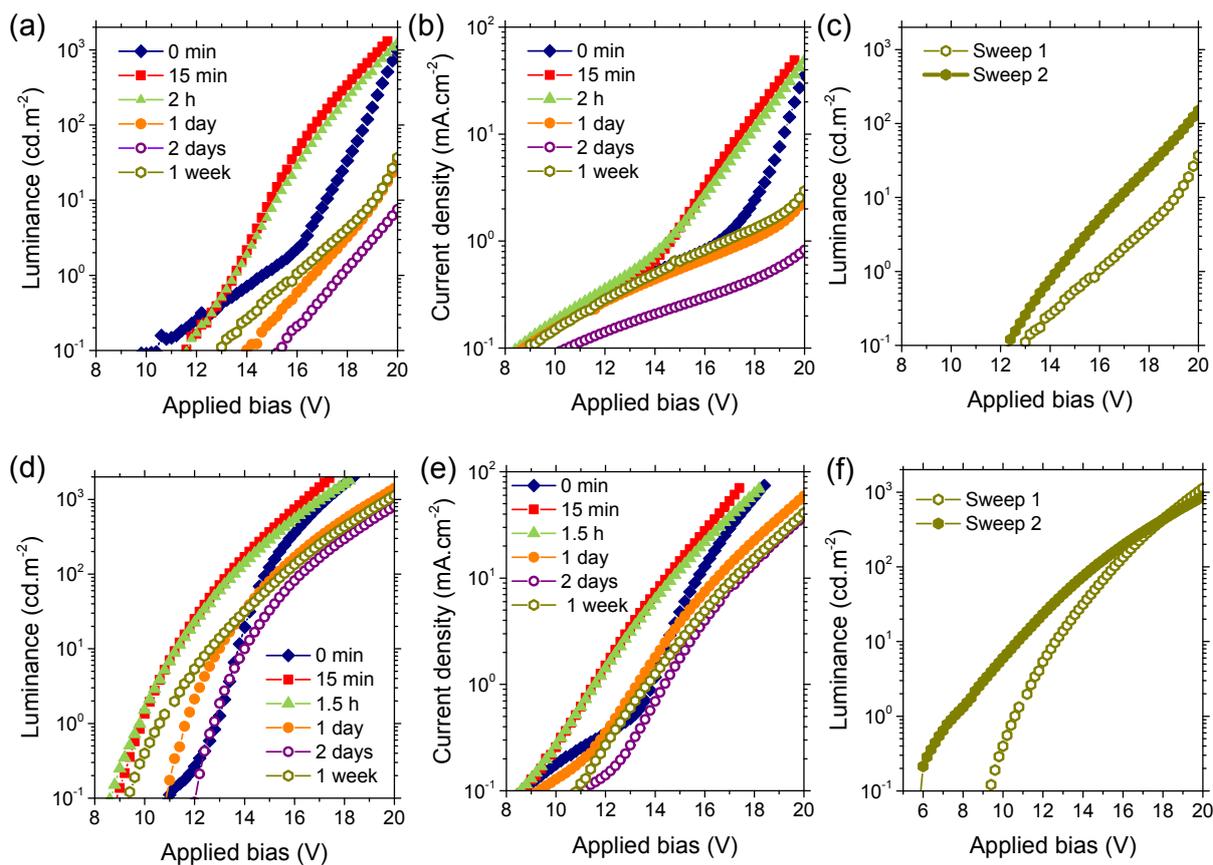


Fig. S4 Repeated voltage sweeps of aryl-F8:0.5 wt.%TFB PLEDs on unannealed ZnO to obtain a measure of stability. (a) Luminance and (b) current density vs. applied bias of PLEDs on ZnO without pre-biasing. After the one week sweep, another sweep was performed and the comparison of the luminance vs. applied bias curves shown in (c). (d) Luminance and (e) current density of PLEDs on ZnO with pre-biasing only before the first sweep at 0 min. These PLEDs were also remeasured after the one week sweep and the comparison of luminance vs. applied bias for the two successive sweeps shown in (f). Curves (a), (b), (d) and (e) show that pre-biasing does not reduce the lifetime of our PLEDs, since the curves after one week matched the original at least as well as those for PLEDs without pre-biasing. They also show that the turn-on voltage increases after one day. Even after storage in air in the dark for a week, biasing the PLED (e.g. through a voltage sweep) reduces the turn-on voltage again.

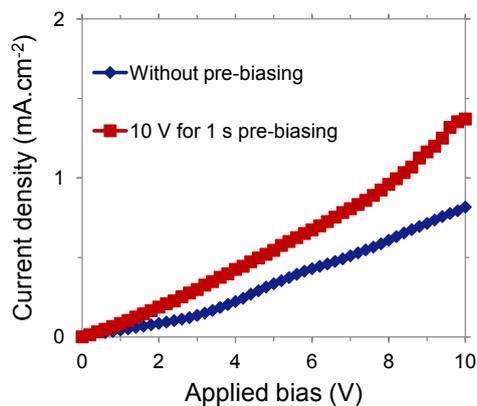


Fig. S5 Influence of pre-biasing on the electron current density of aryl-F8:0.5 wt.%TFB PLEDs with ZnO annealed at 400 °C for 15 min in air. The device structure was ITO/ZnO/Cs₂CO₃/aryl-F8:0.5 wt.%TFB/Ca/Ag.

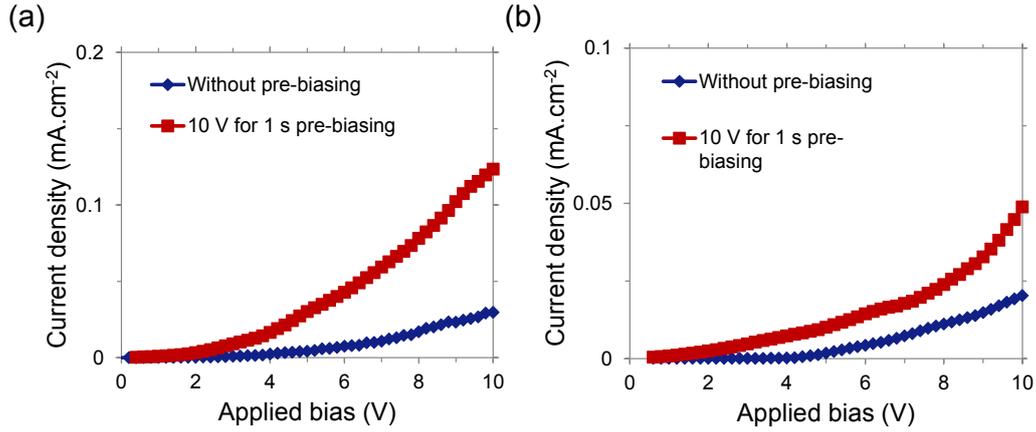


Fig. S6 Current density from electron-only devices based on (a) unannealed and (b) annealed $\text{ZnO}/\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ before and after pre-biasing at 10 V for 1 s. The device structure was ITO/(50 nm) ZnO/(10 nm) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}/\text{Cs}_2\text{CO}_3/\text{aryl-F8:0.5 wt.\%TFB}/\text{Ca}/\text{Ag}$. This shows that the increase in the electron current density after pre-biasing was larger for PLEDs with unannealed $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ than annealed $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$.

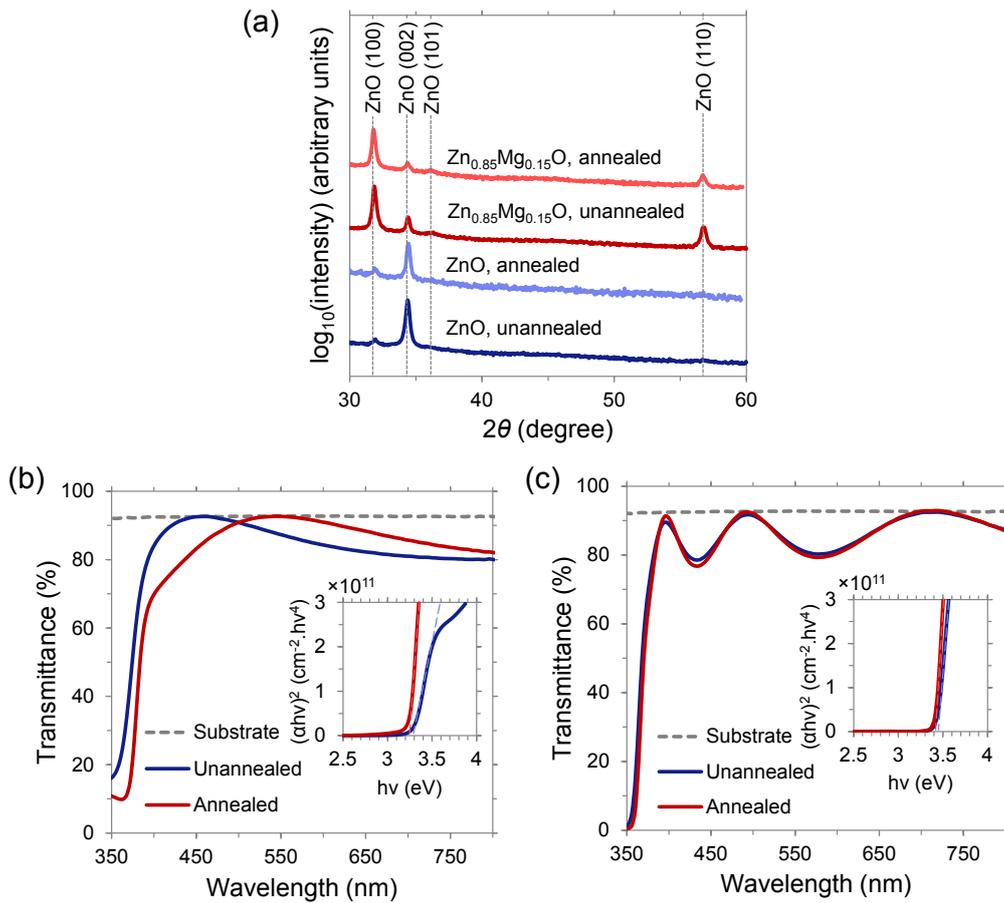


Fig. S7 Influence of annealing on the materials properties of ZnO and $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$. (a) X-ray diffraction measurements. The full width half maximum (FWHM) of the dominant peaks were unchanged after annealing. For ZnO, the (002) peak FWHM remained at 0.2° . For $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$, the (100) peak FWHM remained at 0.2° . Transmittance measurements of (b) ZnO and (c) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ with their corresponding Tauc plots inset. The transmittance of the ZnO films was slightly different due to different interference patterns arising from slightly different thicknesses (140 nm for unannealed ZnO, 125 nm for annealed ZnO). The unannealed $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ film was 320 nm thick and the annealed $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ film 315 nm

thick, and there was no significant change in the transmittance in the visible light range. The Tauc plots show that there was no significant change in the bandgap with annealing. But the steeper onsets of absorption indicate that the disorder in the oxides was reduced after annealing. X-ray diffraction measurements were performed with a Bruker D8 theta/theta instrument using CuK_α radiation that has a wavelength of 1.5406 Å. The transmittance and Tauc plots were obtained using a PerkinElmer Lambda 950 UV-VIS-NIR spectrophotometer with an integrating sphere. All films were deposited onto glass. The transmittance of this glass substrate is shown in parts (b) and (c).

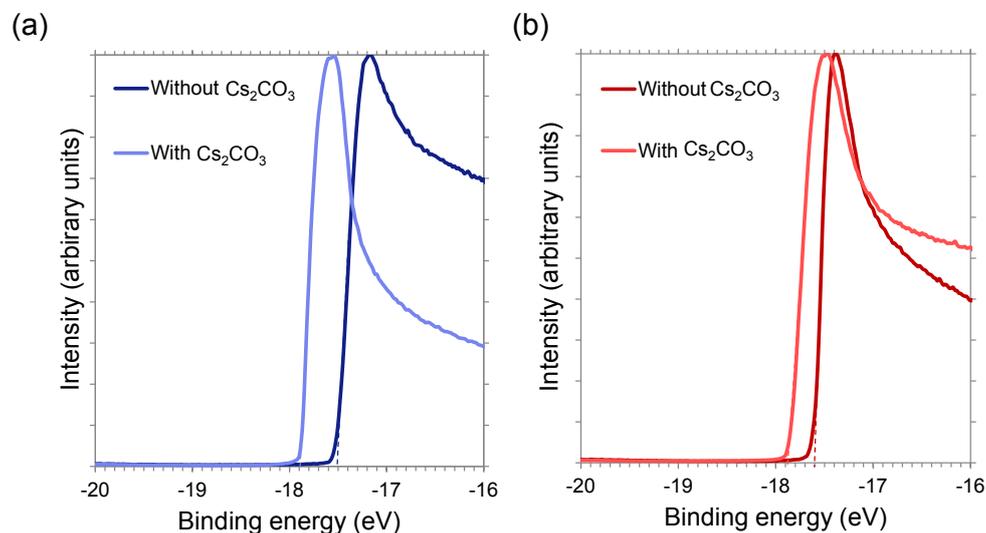


Fig. 8 Ultraviolet photoelectron spectroscopy (UPS) measurements of (a) ZnO and (b) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ with and without Cs_2CO_3 . The Cs_2CO_3 was deposited onto the oxide films by spin-casting at 6000 rpm for 45 s and annealing at 120 °C in a nitrogen glovebox. The photons used in UPS had an energy of -21.22 eV. The extracted binding energies and work functions are shown in Table S1. The absolute value of the oxide work function was decreased with the addition of Cs_2CO_3 .

Table S1 Extracting binding energies from UPS measurements of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with and without Cs_2CO_3 , and the corresponding work functions

Cathode	Cs_2CO_3	Binding energy (eV)	Work function (eV)
ZnO	✓	-17.9	-3.3
	×	-17.5	-3.7
$\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$	✓	-17.8	-3.4
	×	-17.6	-3.6

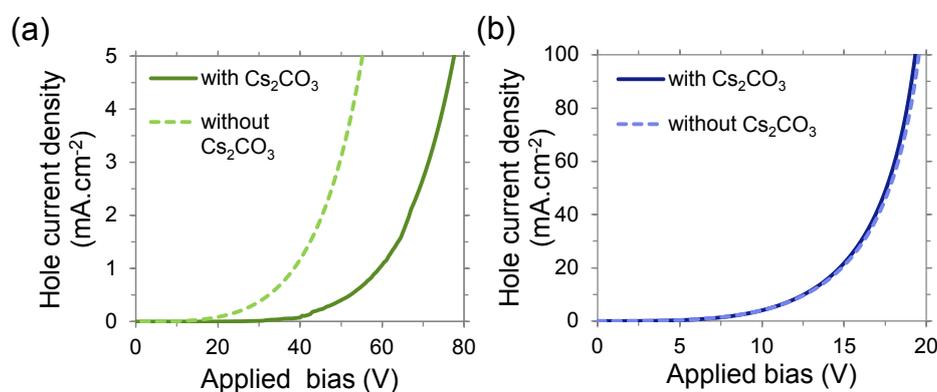


Fig. S9 Comparison of the hole-only current density from (a) 1000 nm thick F8BT PLEDs and (b) 450 nm thick aryl-F8:0.5 wt.%TFB PLEDs with and without a Cs_2CO_3 interlayer. The hole-only device structure was ITO/PEDOT:PSS/((Cs_2CO_3)/polymer layer(s)/ MoO_3 /Au. For the green devices, the polymer layers were 1000 nm F8BT and 200 – 240 nm TFB. For the blue devices, the polymer layer was 450 nm aryl-F8:0.5 wt.%TFB.

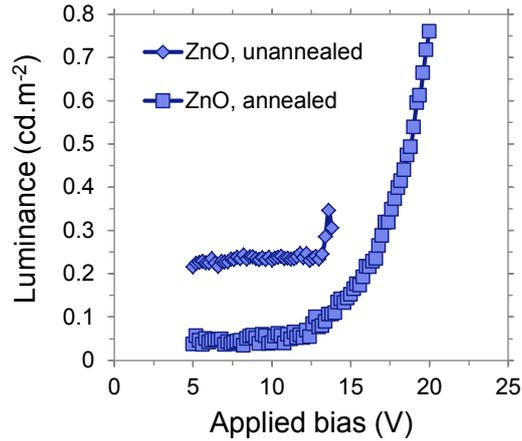


Fig. S10 Luminance vs. applied bias for aryl-F8:0.5 wt.%TFB PLEDs on annealed and unannealed ZnO without a Cs_2CO_3 interlayer. Low PLED performance occurs when Cs_2CO_3 is not used.

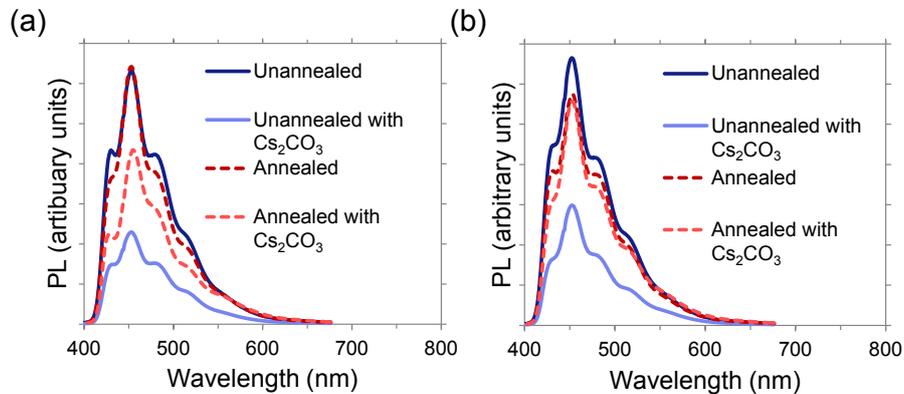


Fig. S11 Photoluminescence (PL) measurements of aryl-F8:0.5 wt.%TFB films on unannealed and annealed (a) ZnO and (b) $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{O}$ with and without Cs_2CO_3 layers between the oxide and polymer. These show that the PL was only significantly lower with the addition of Cs_2CO_3 when the oxide was unannealed. A custom-made setup was used to collect time-integrated PL spectra. A 500 mm SpectroPro2500i spectrograph (Princeton Instruments) and a thermoelectrically cooled PIXIS 100-F CCD camera (Princeton Instruments) were used as the detector. A 407 nm diode laser was used as an excitation source and was driven using a DH400, PicoQuant laser controller. The laser generated pulses with 80 ps FWHM and with a repetition rate of 40 MHz. The samples were excited using 290 μW power.

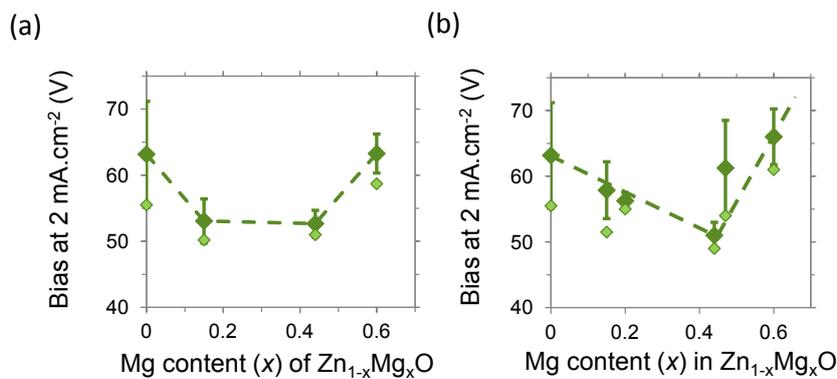


Fig. S12 Bias required to inject $2 \text{ mA}\cdot\text{cm}^{-2}$ into F8BT PLEDs on $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with variable Mg content. (a) Mg is incorporated into the bulk of the metal oxides (*i.e.* 60 nm $\text{Zn}_{1-x}\text{Mg}_x\text{O}$). (b) Mg is incorporated into the surface of the metal oxides (*i.e.* 50

nm ZnO/10 nm $Zn_{1-x}Mg_xO$). The dashed lines are to guide the eye. The PLED architecture was: ITO/AP-CVD metal oxide/ Cs_2CO_3 /(1000 nm) F8BT/(240 nm) TFB/(10 nm) MoO_3 /(50 nm) Au.

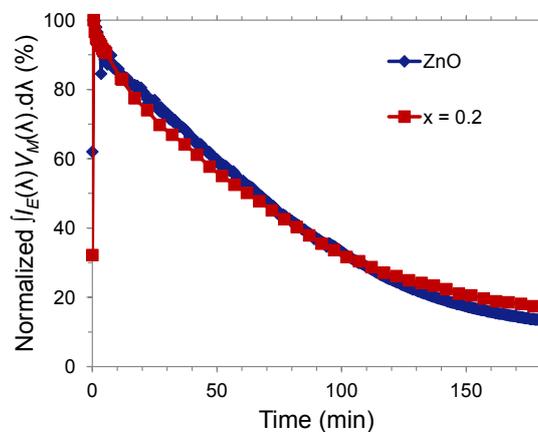


Fig. S13 Stability study of aryl-F8:0.5 wt.%TFB PLEDs on unannealed ZnO and (50 nm) ZnO/(10 nm) $Zn_{0.8}Mg_{0.2}O$. Traces represent integrated electroluminescence spectra (corrected for photopic response), recorded at a constant current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ and normalized to their maximum value. Example spectra are shown in Fig. S14 below. $I_E(\lambda)$ is the electroluminescence intensity. $V_M(\lambda)$ is the photopic luminosity function. This study shows that the stability of the PLEDs was the same when Mg was incorporated into the oxide electron-injector.

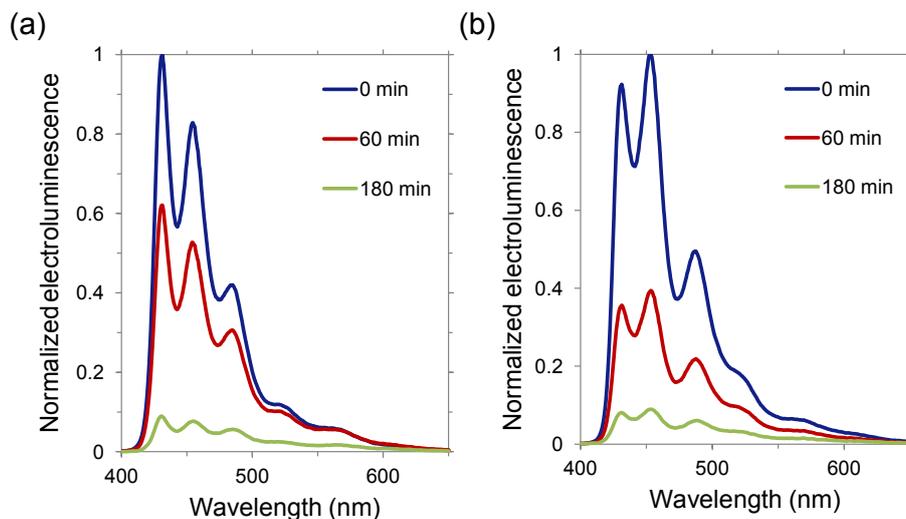


Fig. S14 Electroluminescence spectra normalized to the maximum signal at 0 min for aryl-F8:0.5 wt.%TFB PLEDs with $10 \text{ mA}\cdot\text{cm}^{-2}$ constant current density applied through them. The cathodes were (a) unannealed ZnO and (b) unannealed $Zn_{0.8}Mg_{0.2}O$.

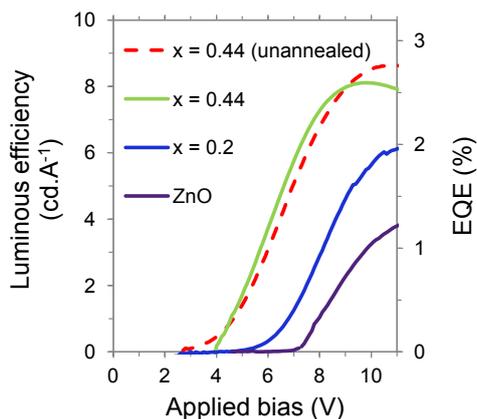


Fig. S15 Reducing the turn-on voltage of thin F8BT polymer LEDs (PLEDs) through Mg incorporation. The oxides were annealed at 400 °C for 15 min after deposition by AP-CVD. For comparison, the performance curve (luminous efficiency and EQE) of PLEDs with unannealed AP-CVD Zn_{0.56}Mg_{0.44}O is also shown. The device structure was ITO/(50 nm) ZnO/(10 nm) Zn_{1-x}Mg_xO/Cs₂CO₃/(150 nm) F8BT/(200 nm) TFB/(10 nm) MoO₃/(50 nm) Au.

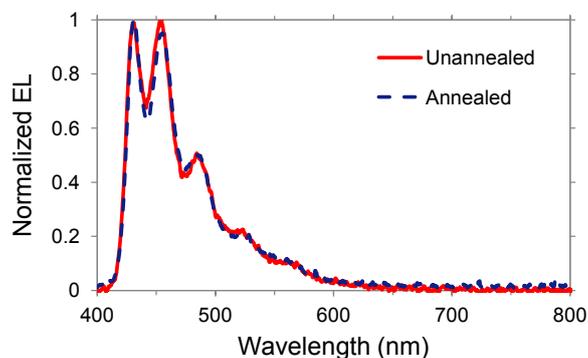


Fig. S16 Electroluminescence spectra of aryl-F8:0.5 wt.%TFB PLEDs on as-deposited and annealed (400 °C for 15 min in air) AP-CVD Zn_{0.85}Mg_{0.15}O biased at 15 V. The spectra were identical with CIE co-ordinates (0.16, 0.08).

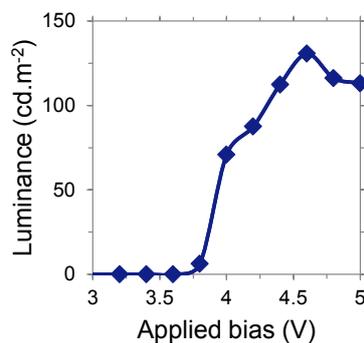


Fig. S17 Luminance vs. applied bias of aryl-F8:0.5 wt.%TFB PLED with 80 nm thick emitter layer on unannealed Zn_{0.8}Mg_{0.2}O cathode. This thin PLED had a low turn-on voltage of 3.7 V.

Reference

- 1 R. L. Z. Hoye, B. Ehrler, M. L. Böhm, D. Muñoz-Rojas, R. M. Altamimi, A. Y. Alyamani, Y. Vaynzof, A. Sadhanala, G. Ercolano, N. C. Greenham, R. H. Friend, J. L. MacManus-Driscoll, and K. P. Musselman, *Adv. Energy Mater.*, 2014, **4**, 1301544.
- 2 M. Lu, P. De Bruyn, H. T. Nicolai, G.-J. A. H. Wetzelaer, and P. W. M. Blom, *Org. Electron.*, 2012, **13**, 1693–1699.