

Supporting Information

Improved Thermal Stability and Operational Lifetime of Blue Fluorescent Organic Light Emitting Diodes by using A Mixed Electron Transporting Layer

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Materials and sample preparation

The silicon wafer substrates were blown dry with nitrogen gas and then treated by UV–ozone for 15 min prior to loading into a thermal evaporation system. Each film of ≈ 200 nm was deposited by a thermal co-evaporation at a base pressure of $\approx 10^{-7}$ torr. The mixing percentage was controlled from the deposition rates of two source materials, which were individually monitored by two quartz crystal microbalances. The sum of deposition rates of the two materials was kept at $\approx 2 \text{ \AA s}^{-1}$. The mixing percentage presented in the manuscript is volume percentage unless specified otherwise. Both encapsulated and as-deposited samples were produced, and the encapsulation process was conducted under vacuum.

The glass transition temperature measurements

The spectroscopic ellipsometer (Nano-View, SE MG-1000) is equipped with a custom-built closed chamber that enables control from a vacuum ($\approx 10^{-2}$ torr) to nitrogen-rich environments.¹⁻² Inside the chamber, a vacuum grease (Krytox LVP high-vacuum grease) was applied between the silicon wafer and the temperature-controlled copper plate to ensure a good thermal connection between the sample and the plate. In addition, the sample was pressured down with a copper block which has openings in the light paths to have thermal equilibrium between the temperature control element and the sample surface. The

sample was heated and cooled in the range of $T_g \pm 20\text{-}25^\circ\text{C}$ and to achieve a fast cooling rate up to room temperature, cooled air ($\approx 5^\circ\text{C}$) was passed through the temperature-controlled plate using a custom-built thermoelectric cooler (TEC) based air cooler. The ellipsometry data were measured from the wavelength of 300 to 885.6 nm to avoid degradation of the organic material in the UV range.

To determine the glass transition temperature (T_g), the sample was heated and cooled at the rate of $10^\circ\text{C min}^{-1}$ and 5°C min^{-1} , respectively. Typically, three temperature cycles were performed and T_g was determined from the cooling scans after the first run. For each scan, film thickness was normalized at the end of the cooling cycle and averaged. Temperature dependent thickness data in the range of $10 - 15^\circ\text{C}$ at the low and high ends of the temperature scan were linearly fitted and the T_g was determined as the interception temperature of these two fitted lines. From the slopes of each lines in the glass and supercooled liquid region, the thermal expansion coefficients were calculated using $\alpha = 1/h_{T_g} (dh/dT)$,³⁻⁴ where, h_{T_g} is the thickness at T_g . During the temperature scans, the ellipsometric parameters (Δ , Ψ) were measured every 10 second at a fixed incidence angle of 70° . The delta (Δ) and psi (Ψ) data were fitted to a three-layer model consisting of a silicon layer as a substrate, 2 nm thick native oxide layer, and a transparent layer to account for the film of interest. The temperature-dependent index of refraction, $n(T)$, and temperature-dependent thickness, $h(T)$, of the layer were fitted to a Cauchy model ($n(\lambda) = A + B/\lambda^2$), and the imaginary part of the index of refraction, K was assumed to be zero.⁵⁻⁶

In the preparation of mixed film in the current study, the mixing percentage was controlled by the deposition rate, which makes the primary control of mixing as volume percentage. From the reported density of BPhen (1.24 g cm^{-3}),⁷⁻⁸ Liq density was estimated (1.16 g cm^{-3}) by comparing thicknesses of the deposited films of pristine BPhen and Liq at the same deposition condition. These densities are utilized to convert weight and mole fractions in the Fox⁹ ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$) and Gibbs-DiMarzio¹⁰⁻¹¹ ($T_g = n_1T_{g1} + n_2T_{g2}$) equations to the volume fractions and vice versa. Here, w_x , n_x , and $T_{g\ x}$ are the weight fraction, mole fraction, and T_g of x component, respectively.

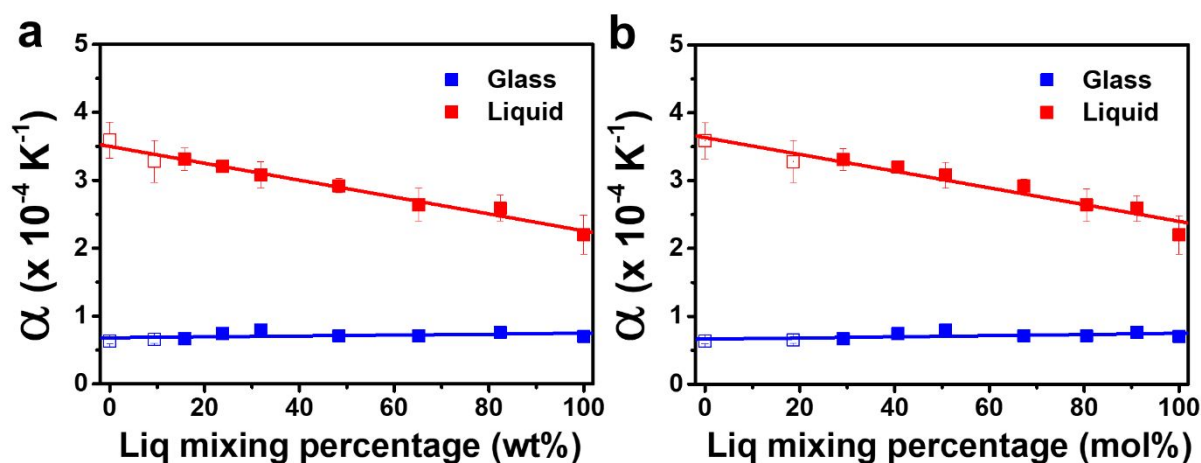


Figure S1. The thermal expansion coefficients for the pristine and mixed films as a function of (a) weight and (b) mol percentage, respectively. The red and blue lines in the fig. are the linear fits to the data.

Table S1. Liq mixed BPhen T_g and Thermal expansion coefficient (α) values

Liq mixing percentage	T_g (K)	Thermal expansion coefficient (α)	
		Liquid ($\times 10^{-4}$) K^{-1}	Glass ($\times 10^{-5}$) K^{-1}
0%	335.2 ± 0.7 (T_f)	3.59 ± 0.27	6.33 ± 0.38
10%	343.4 ± 0.5 (T_f)	3.28 ± 0.31	6.55 ± 0.53
17%	347.4 ± 1.6	3.30 ± 0.16	6.63 ± 0.53
25%	353.9 ± 1.5	3.20 ± 0.07	7.43 ± 0.28
33%	357.8 ± 2.1	3.08 ± 0.19	7.97 ± 0.55
50%	363.3 ± 0.7	2.92 ± 0.10	7.12 ± 0.28
67%	367.1 ± 0.7	2.64 ± 0.24	7.11 ± 0.79
83%	368.1 ± 0.8	2.59 ± 0.19	7.62 ± 0.37
100%	370.9 ± 2.2	2.20 ± 0.29	7.03 ± 0.56

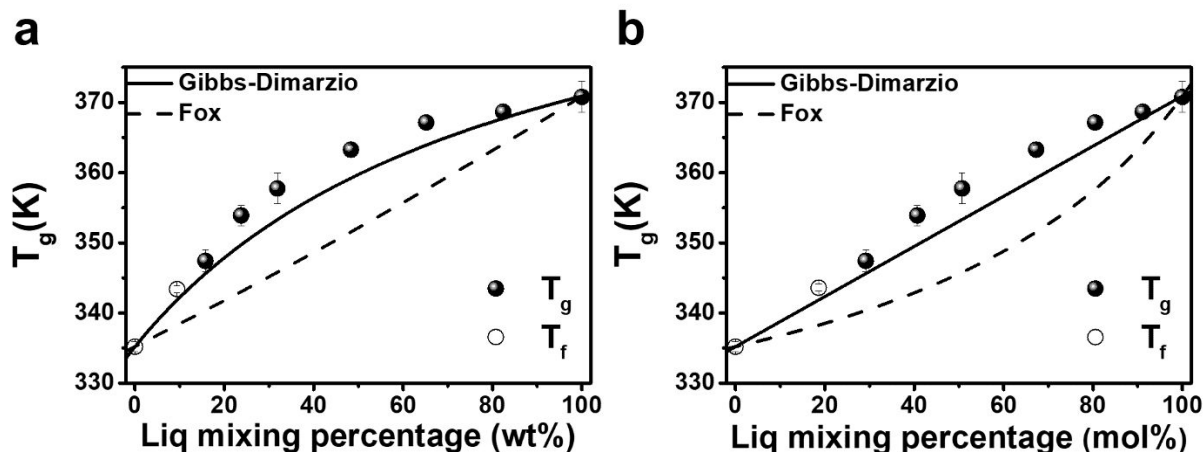


Figure S2. The glass transition temperatures of mixed films with varying compositions are expressed in terms of (a) weight and (b) mole percentages, respectively. The solid and dashed lines are Gibbs-DiMarzio and Fox predictions of glass transition temperatures (T_g) for amorphous mixture films.

Surface characterizations

To investigate the morphological stability of mixed films, custom-built reflection polarization optical microscope and atomic force microscope (AFM) were utilized to monitor crystallization behavior of pristine BPhen and the mixed films. Reflection polarization optical microscope equipped with a closed chamber for temperature and environmental controls enables to control from room temperature to ≈ 473 K and from ambient to vacuum ($\approx 10^{-2}$ torr) conditions. An incident unpolarized light from a fiber optic light source (Light Bank LS-F100HS) was collimated and polarized (Thorlabs, LPVISE100-A). Polarized incident light was reflected by a plate beam splitter (50:50) (Thorlabs, BSW10R) at the angle of 45° and focused to the back of the objective lens (OLYMPUS UPlanSAPO, 4X) to achieve a wide field configuration. Reflected light from a sample film was collected with the same objective lens and passed through the plate beam splitter and an analyzer (Thorlabs, LPVISE100-A) before focusing onto a CCD camera (Thorlabs, DCU223C). Both polarizer and analyzer were placed in rotation mounts to adjust orthogonal polarization between the incident and reflected light

Atomic Force Microscope (AFM; NX-10 AFM, Park Systems). The area of $10 \times 10 \mu\text{m}^2$ was scanned with a rate of 0.3 Hz in non-contact tapping mode using a cantilever (PPP-NCHR-10, Nanosensors) which has a resonance frequency of 204 - 497 kHz and the force constant of 10 - 130 Nm^{-1} . The root-mean-

square (RMS) roughness of samples was acquired by analyzing $4 \times 4 \mu\text{m}^2$ area out of the $10 \times 10 \mu\text{m}^2$ image.

Table S2. Root-mean-square (RMS) roughness values for the pristine BPhen and mixed films with various mixing percentages and storage conditions.

Vol % of Liq	Root-mean-square (RMS) roughness		
	Vacuum, $T = T_g$ (nm)	Ambient, $T = T_g$ (nm)	Ambient, $T > T_g$ (nm)
0%	46.2 ± 2.7	43.2 ± 2.3	30.2 ± 0.7
0.5%	46.2 ± 2.4	42.8 ± 2.1	43.6 ± 9.4
1%	45.0 ± 2.0	47.8 ± 1.6	34.2 ± 4.1
5%	0.3 ± 0.1	48.9 ± 3.6	47.6 ± 4.8
10%	0.3 ± 0.1	0.3 ± 0.1	33.1 ± 4.0
17%	0.4 ± 0.1	0.3 ± 0.1	0.8 ± 0.1
33%	0.4 ± 0.1	0.4 ± 0.1	1.0 ± 0.1
50%	0.3 ± 0.1	0.6 ± 0.1	1.2 ± 0.1

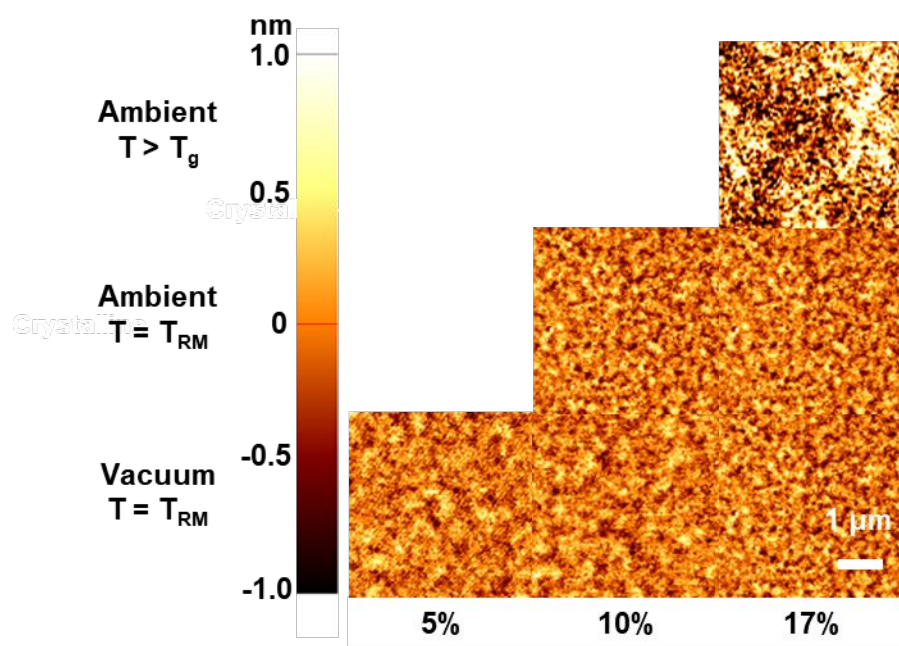


Figure S3. AFM images of films that appears to be amorphous in the reflection microscorpy with various compositions and under different storage conditions.

In X-ray photoelectron spectroscopy (XPS), the kinetic energy of the photoelectrons of the sample produced by Mg K-alpha radiation (1253.6 eV) was measured using a concentric hemispherical electron

analyzer (CHA, PHOIBOS 150 1D-DLD, SPECS, Germany) under ultrahigh vacuum condition ($\approx 5.0 \times 10^{-10}$ torr). The binding energy of each spectrum was calibrated by C 1s core level (graphite carbon, 284.6 eV), and the peak intensities of N 1s and Li 1s were mathematically manipulated to correspond the number of N and Li atoms per unit volume in each mixture (Table S2). Spectra were all subtracted by Shirley-type background.

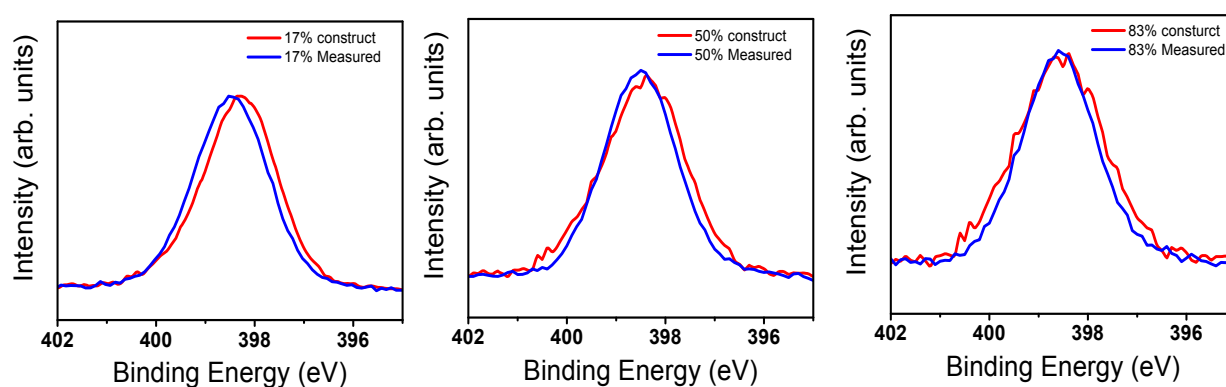


Figure S4. Measured N 1s spectra of mixture films with 17, 50, and 83% composition of Liq in comparison with the respective mathematically constructed spectra using pristine Liq and Bphen spectra as components.

Table S3. The mathematical parameters for the intensities of N 1s and Li 1s XP spectra in Figure 1.

Liq			BPhen	Atomic ratio in the mixture (Intensity ratio in XP spectra)	
*100 ml Standard	Li mass(g)	N mass(g)	N mass (g)	N	Li
0%	0	0	10.4	0.96	0
17%	0.9	1.8	8.7	0.97	0.17
50%	2.7	5.4	5.2	0.98	0.50
83%	4.4	8.9	1.8	0.99	0.83
100%	5.3	10.8	0	1	1

Device Fabrication and Measurements.

Prior to deposition, the ITO substrates were thoroughly cleaned in an ultrasonic bath using detergents and deionized water subsequently. The pre-treatment of the substrates was carried out in a clean room of class 1000 to ensure the least amount of particle or moisture on the substrates. The current, voltage, and

luminance of the devices were measured using a Keithley 2400 Source-Meter and Topcon SR-3AR spectroradiometer.

Encapsulation procedure

After cleaning an encapsulation glass, epoxy resin (Nagase, XNR5570) was applied to the edge of the glass and attached to the substrate followed by curing with UV light (365 nm, 200 Wcm⁻²) for 5 min. The deposited film area was protected with aluminum foil during UV curing.

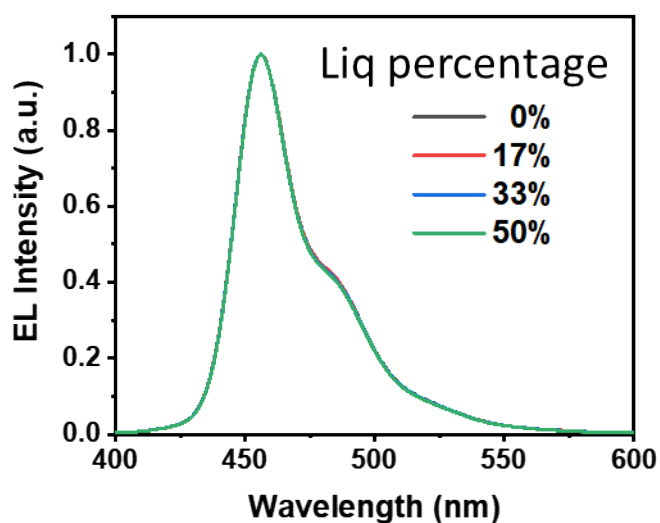


Figure S5. The electroluminescence (EL) spectra ($\lambda_{\text{max}} = 456$ nm) of the blue devices with different Liq percentage in the mETL.

Table S4. The driving voltage at 25 mA cm⁻² according to the annealing temperatures ranging from room temperature to 393.15 K for the devices with different mixing ratio of BPhen and Liq in the mETLs.

Annealing temperature (K)	Driving voltage (V)			
	0% of Liq	17% of Liq	33% of Liq	50% of Liq
298.2	5.0	6.1	5.8	5.8
323.2	3.6	5.5	5.8	5.7
343.2	4.1	4.0	5.7	5.8
363.2	5.2	5.6	5.5	6.1
373.2	5.3	5.7	5.5	6.2
383.2	-	6.1	6.2	6.5
393.2	-	-	-	8.0

Table S5. The luminance at 25 mA cm⁻² according to the annealing temperatures ranging from room temperature to 393.15 K for the devices with different mixing ratio of BPhen and Liq in the mETLs.

Annealing temperature (K)	Luminance (cd/m ²)			
	0% of Liq	17% of Liq	33% of Liq	50% of Liq
298.2	1168	938	861	846
323.2	1046	978	866	851
343.2	137	1062	930	895
363.2	56	137	930	994
373.2	55	136	1315	992
383.2	-	3	140	1059
393.2	-	-	-	47

Table S6. The external quantum efficiency (EQE) at 25 mA cm⁻² according to the annealing temperatures ranging from room temperature to 393.15 K for the devices with different mixing ratio of BPhen and Liq in the mETLs.

Annealing temperature (K)	EQE (%)			
	0% of Liq	17% of Liq	33% of Liq	50% of Liq
298.2	5.3	4.3	3.9	3.9
323.2	4.7	4.5	3.9	3.9
343.2	0.4	4.8	4.2	4.1
363.2	0.1	0.3	4.2	4.6
373.2	0.1	0.3	6.0	4.5
383.2	-	0.01	0.3	4.8
393.2	-	-	-	0.1

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