Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information (S3) - Computational Simulations

The basic semiconductors equations consist of three partial differential equations – Poisson's equation and continuity equations for electrons and holes (See Equations (1) - (3), respectively). These equations together with boundary conditions and a net recombination function form a mathematical model (Drift-Diffusion model) for the charge dynamics within the OLED.

$$\Delta V - \frac{q}{\varepsilon}(n-p) = 0 \tag{1}$$

$$\frac{1}{q}\nabla J_n - R(V,n,p) = \frac{\partial n}{\partial t} \tag{2}$$

$$\frac{1}{q}\nabla J_p - R(V,n,p) = \frac{\partial p}{\partial t} \tag{3}$$

$$J_n = qD_n\nabla n - q\mu_n n\nabla V \tag{4}$$

$$J_p = qD_p\nabla p + q\mu_p p\nabla V \tag{5}$$

$$R = \gamma\left(np - n_{int}^2\right) \tag{6}$$

$$\mu = \mu_0 \exp\left(\sqrt{\frac{q^3 E}{4\pi k_B^2 T^2 \varepsilon}}\right) \tag{7}$$

The parameters in Equations (1) - (7) are as follows: V is the electrostatic potential distribution; q is the elementary electric charge; ε is the dielectric constant; n and p are the electron and hole densities, respectively. Under a steady-state condition, Equations (2) and (3) become time-independent, namely, $\frac{\partial n}{\partial t}, \frac{\partial p}{\partial t} = 0$, and the continuity equations are represented by the drift-diffusion currents for electrons and holes, J_n and J_p (Equations (4) and (5), respectively), and by the recombination rate R (Equation (6)). $D_{n,p}$ are the carrier diffusion coefficients, and $\mu_{n,p}$ are the Poole-Frankel field-dependent mobilities of the electrons/holes (See Equation (7)), where μ_0 is the zero-field mobility, and E is the electric field. The recombination rate was modeled according to Langevin's theory with a recombination strength $\gamma = q\langle\mu\rangle/\langle\varepsilon\rangle$, where the angle brackets represent the mean values of the parameter in the blend active layer. The intrinsic carrier density is given by $n_{int} = N_c exp\left(-E_{gap}/V_T\right)$, where N_c is the conduction and valence band effective densities of states; E_{gap} is the bandgap between the blend materials; and

$V_T = k_B T/q$ is the thermal voltage, where k_B is the Boltzmann's constant and T is the absolute temperature.

The injection currents were modeled using a weighted expression as shown in Equation (8) of both Scott-Malliaras (Equations (9) - (10)) and Fowler-Nordheim Tunneling (Equation (11)) currents.

$$J_n^{cat} = w_{FN} J_{FN,n}^{cat} + (1 - w_{FN}) J_{SM,n}^{cat} \quad (8)$$

$$J_{SM,n}^{cat} = A_n^* T^2 \left[N_0 \exp\left(-\frac{\phi_{B,n}}{k_B T} + \sqrt{f} \right) - n \left(\frac{1}{\psi^2} - f \right) / 4 \right] \quad (9)$$

$$J_{SM,p}^{an} = A_p^* T^2 \left[P_0 \exp\left(-\frac{\phi_{B,p}}{k_B T} + \sqrt{f} \right) - p \left(\frac{1}{\psi^2} - f \right) / 4 \right] \quad (10)$$

$$J_{FN}^{cat} = C_1(\phi_{B,n}, \varepsilon_{cat}, B_{FN}) E^2 \cdot e^{-\frac{C_2(\phi_{B,n}, \varepsilon_{cat}, A_{FN})}{E}} \quad (11)$$

The additional parameters in Equations (8) - (11) are as follows: J_n^{cat}, J_p^{an} are the electron/hole current densities at the cathode/anode, respectively; w_{FN} is the weighting factor of the Fowler-Nordheim tunneling current and $(1 - w_{FN})$ is the weighting factor of the Scott-Malliaras injection currents. $A_{n/p}^* = 16\pi\varepsilon_0\varepsilon_1\mu_{n(p)}K_B^2/(q^* q^2)$ is the effective Richardson constant; N_0 and P_0 are the electrons and holes density of states; $\phi_{B,n/p}$ are the barrier height for the electrons/holes; f is the reduced electric field and ψ is given by $\psi = f^{-1} + f^{-1/2} - f^{-1}\sqrt{1 + 2\sqrt{f}}$. A_{FN} and B_{FN} in C_1, C_2 are constants fitting parameters that relate to the approximation of the barrier triangular shape, and that the tunneling occurs only through part of the injection layer.

The model was used to simulate the steady-state performance of polyfluorene-based OLEDs with different thicknesses of a LiF injection layer. The structure of the pristine OLED consists of ITO(150nm)/PEDOT:PSS(25nm)/PFO:F8BT blend(80nm)/Ag(90nm). The structure of the modified devices included the insertion of an ultra-thin LiF layer between the polymer active layer and the Ag

cathode, the tested thicknesses of the LiF injection layers were 1nm, 2nm and 3nm. The material properties used in our simulation for the pristine device are summarized in Table S. 1.

Table S. 1: Device parameters used in the simulation for the pristine OLED

Parameter	**Symbol**	**Value**
Active layer thickness ($\boldsymbol{nm}$)	L	80
Active layer dielectric constant ($\boldsymbol{F/cm}$)	$\langle\varepsilon\rangle$	3
Electron zero-field mobility ($\boldsymbol{cm^2/V\ s}$)	$\mu_{0,n}$	10^{-5}
Hole zero-field mobility ($\boldsymbol{cm^2/V\ s}$)	$\mu_{0,p}$	10^{-5}
Effective density of states ($\boldsymbol{cm^{-3}}$)	N_0/P_0	10^{20}
Barrier for electrons at the cathode ($\boldsymbol{eV}$)	$\phi_{B,n}^{cat}$	0.435

The extracted steady-state fitting parameters for devices with different thicknesses of the LiF layer are given in the Table S. 2.

Table S. 2: Steady-state fitting parameters for devices with different thicknesses of the LiF layer

Cathode	Fitting Parameters		
	ϕ_B $[eV]$	w_{FN}	ε_{cat}
Ag	0.435	8e-6	Metal - Ag
1nm LiF/ 90nm Ag	0.237	0.9	20
2nm LiF/ 90nm Ag	0.495	0.2	13
3nm LiF/ 90nm Ag	0.514	1e-4	9

Upon insertion of 1nm of the LiF layer, the effective barrier height is reduced by ~200meV. However, a further progressive increment of the insulating LiF layer thickness leads to a progressive increment in the height of the barrier. Such behavior was observed with typical

changes in the effective barrier height in the range of up to 500meV, as shown in previous studies. As mentioned, the effect of the LiF insulating layer is often modeled by electron tunneling. The weighting factor of the injection current for each of the devices is shown in Table II and is denoted w_{FN}. The pristine device with no LiF layer exhibits no tunneling behavior and can be fitted using only the Scott-Malliaras approach. In contrast, the injection current in the OLED with the higher injection efficiency (1nm of LiF layer) is governed mostly by tunneling, based on the Fowler-Nordheim approach. As we increase the LiF thickness, the effect of tunneling is gradually reduced until this mechanism becomes negligible in the device with the 3nm LiF layer as the insulating layer is relatively thick and does not facilitate tunneling. Lastly, the dielectric constant at the interface is modified relative to the pristine cathode with permittivity of a pure Ag bulk. However, the deposition of an ultra-thin layer of LiF does not form continuous and homogenous layer that fully coverages the surface, but instead, the LiF molecules form island clusters on the active polymer layer. Therefore, the dielectric constant at the interface is modified and depends on the thickness of the LiF layer until it reached to its bulk value ($\varepsilon_{LiF} = 9$).