Organic Semiconductors

Efficient Charge Carrier Injection and Balance Achieved by Low Electrochemical Doping in Solution-Processed Polymer Light-Emitting Diodes

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Charge carrier injection and transport in polymer light-emitting diodes (PLEDs) is strongly limited by the energy level offset at organic/(in)organic interfaces and the mismatch in electron and hole mobilities. Herein, these limitations are overcome via electrochemical doping of a light-emitting polymer. Less than 1 wt% of doping agent is enough to effectively tune charge injection and balance and hence significantly improve PLED performance. For thick single-layer (1.2 µm) PLEDs, dramatic reductions in current and luminance turn-on voltages ($V_1 = 11.6$ V from 20.0 V and $V_1 = 12.7$ V from 19.8 V with/without doping) accompanied by reduced efficiency roll-off are observed. For thinner (<100 nm) PLEDs, electrochemical doping removes a thickness dependence on V_1 and V_1 , enabling homogeneous electroluminescence emission in large-area doped devices. Such efficient charge injection and balance properties achieved in doped PLEDs are attributed to a strong electrochemical interaction between the polymer and the doping agents, which is probed by in situ electric-field-dependent Raman spectroscopy combined with further electrical and energetic analysis. This approach to control charge injection and balance in solution-processed PLEDs by low electrochemical doping provides a simple yet feasible strategy for developing high-quality and efficient lighting applications that are fully compatible with printing technologies.

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1. Introduction

Polymer light-emitting diodes (PLEDs), consisting of solution-processed π -conjugated polymers (π -CPs) sandwiched between high- and low-work-function contact electrodes, are a well-established technology for high-quality, low-cost, flexible, and transparent display applications.^[1] To achieve high brightness and high efficiency, PLEDs require ohmic contact between the electrodes and semiconducting layer(s), where the smallest possible energy level offset is required to ensure efficient charge injection and charge balance.^[2] The development of solution-processed π -CPs with a sufficiently high or low work function (WF) presents a significant challenge, which typically results in an energy level offset between the work function of the metal electrode (or organic layers) and the highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) level of π -CPs.^[3–5]

There has been considerable effort devoted to overcoming these large energy

level offsets by inserting additional charge injection and transport layers. These layers have included a wide range of semiconducting and conducting polymers (e.g., poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), poly[(9,9dioctylfluorenyl-2,7-diyl)-*co*-(4,4'-(*N*-(4-sec-butylphenyl) diphenylamine)] (TFB)), and conjugated polyelectrolytes (e.g., poly[9,9bis[6-(*N*,*N*,*N*-trimethylammonium)-hexyl] fluorene-alt-co-phenylene] tetrakis(imidazolyl)borate) as well as metal oxides (e.g., molybdenum oxide, vanadium oxide, and zinc oxide).^[5-12] The chemical doping of π -CPs with molecular Lewis-acid dopants can also be used to control the charge carrier density and thus the electronic energy levels of π -CPs.^[13] Although the combined approach appears effective for reducing the charge injection barrier, conventional PLEDs still suffer from low device efficiency, thickness-dependent turn-on voltage, and efficiency roll-off due to poor charge injection and balance.^[14–16]

A promising approach for highly efficient PLED applications is a blend system of π -CPs with liquid-state electrolytes consisting of two asymmetrical ions of opposite charges (i.e., ionic liquids), in which the charge carrier density of the π -CPs can be





Figure 1. a) Chemical structures of F8BT and EDA molecules and the conventional PLED architecture of ITO/PEDOT:PSS/TFB/neat F8BT(or F8BT:EDA)/Ca/Al. b) Energy level diagram of PLED showing a large HOMO level offset for hole injection ($\Delta E_h \approx 0.5 \text{ eV}$) at the ITO/PEDOT:PSS/TFB and F8BT interface.

modulated by electrochemical doping under electric fields.^[17-22] However, the differences in surface energy and hydrophobicity between the π -CPs and liquid-state electrochemical doping agents (EDAs) necessitate high dopant concentrations to obtain sufficient interfacial areas between the two components. In addition, the PLEDs comprising π -CPs and liquid-state electrochemical dopants often show a slow turn-on or need prebiasing due to the slow ion diffusion and unstable motion of the liquidstate EDAs.^[7,16,23] These material properties raise concerns about the structural orientation of π -CPs and the morphology of the layers in PLEDs, which may also affect color uniformity and device efficiency. Therefore, the development of a solidstate EDA with a minimal surface energy difference from that of π -CPs would ensure fast, stable ion diffusion over a large interface, enabling efficient charge injection and balance for PLED applications with high-quality brightness and long-term device stability.

Herein, we demonstrate a novel solid-state EDA that can form a homogeneous blend system with π -CPs and control the interfacial energetics via electrochemical doping. We find that PLEDs with a low level of EDA (0.5 wt%) decrease turn-on voltages dramatically. Such reduction in the turn-on voltage is more pronounced for thick devices (>1 μ m), which generally show much poorer charge injection than for thin devices. For example, the incorporation of EDA into π -CPs devices with 1.2 µm thick electroactive layer reduces the current and luminance turn-on voltages by 8.4 and 7.1 V respectively (from 11.6 to 20.0 V for current turn-on and from 12.7 to 19.8 V for luminance turn-on with/without EDA). On the other hand, for thinner (<100 nm) π -CPs:EDA PLEDs, negligible thickness-dependent turn-on voltages with minimized efficiency roll-off and extended half-life are observed. The optimized π -CPs:EDA PLEDs show homogeneous emission in large-area devices $(1 \times 1 \text{ cm}^2)$. The significantly improved performance of π -CPs:EDA PLEDs is attributed to effectively controlled charge injection and balance properties of π -CPs by EDA via electrochemical doping.

2. Preparation of Poly(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole) (F8BT):EDA Blends for PLEDs

The chemical structures of the π -CPs (here, the polyfluorene copolymer F8BT and the solid-state EDA (here, 1,12-alkylimidazolium (+) hexafluorate (–)) are shown in **Figure 1**a. The EDA was strategically tailored to contain a long alkyl chain in the cation, which can minimize the surface energy difference between the F8BT and EDA molecules.^[22]

We first investigated the effects of EDA blending ratio on F8BT ($M_n \approx 21$ K) PLEDs. Devices fabricated with 0.3, 0.5, 1, 3, and 5 wt% EDA blended with F8BT were tested in a conventional device architecture indium-tin-oxide (ITO)/ PEDOT:PSS/TFB/F8BT:EDA/Ca/Al. Among the devices tested, F8BT PLEDs with a small amount of EDA (0.5 wt%) exhibited the best device performance. Such a low concentration of EDA did not affect the morphology and optical properties of F8BT films, as evidenced by atomic force microscopy (AFM), UV-vis absorption, photoluminescence (PL), PL quantum yield (PLQY), and PL transient characteristics (more details are shown in Figures S1-S4, Supporting Information).^[24] We also found that the effect of EDA doping becomes more prominent when blended with low molecular weight F8BT such as $M_n = 9$, 21, and 33 K, as opposed to F8BT with a higher molecular weight over 64 K (Figure S5, Supporting Information). These molecular weight dependent F8BT:EDA PLED performance can be understood from different mixing of small EDA molecules in various polymer matrix, e.g. vertical versus lateral distributions of small EDA molecules in blends, determining preferential interfacial versus bulk doping characteristics throughout the active layer.^[25] Based on these preliminary studies, we selected 0.5 wt% EDA and 21 K F8BT for further investigation, to understand the mechanism behind the improved device performance observed in F8BT PLEDs. We have considered not only thin (<100 nm) devices but also thick (<1 µm) devices, which are more compatible with printing technologies.

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Figure 2. a,b) J-V-L characteristics of neat F8BT and F8BT:EDA PLEDs with different thicknesses ranging from 60 to 112 nm. c) J-V-L characteristics of 1.2 μ m thick devices with/without EDA. d) Turn-on voltages for luminance (V_L) as a function of thicknesses for neat F8BT and F8BT:EDA PLEDs. Note: The left Y-axis and right-Y-axis are for thin devices (60–200 nm) and thick devices (650–1200 nm), respectively. The inset graph shows the reduced turn-on voltages by EDA (ΔV_L) as a function of thickness.

The energy diagram in Figure 1b illustrates the large energy level offset between the ITO/PEDOT:PSS/TFB hole-injection/ transport layer (5.3 eV) and the active layer (5.8 eV), which results in poor hole injection. On the other hand, there is a desirable ohmic contact between the F8BT layer and the Ca/Al cathode, which results in efficient electron injection.^[24] In addition, there is three-order-of-magnitude different hole ($\mu_h \approx 1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electron ($\mu_e \approx 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) mobilities reported for the F8BT, which results in poor charge balance and limits charge carrier recombination and emission.^[15,24,26]

3. Device Characteristics of PLEDs Incorporating EDAs

The current density–voltage–luminescence (J-V-L) characteristics of PLEDs depending on a range of active layer (neat F8BT or F8BT:EDA) thicknesses are shown in **Figure 2**a,b. The current

density and luminance of the neat F8BT PLEDs with thicknesses from 60 to 112 nm under low voltage (~2.6 V) decreased more than three orders of magnitude with a significant increase of the luminance turn-on voltages from 2.0 to 2.9 V. However, compared to those of the neat F8BT PLEDs, the *J*–*V*–*L* characteristics and turn-on voltage of the F8BT:EDA PLEDs showed almost negligible thickness dependence. We found that such improvements in *J*–*V*–*L* characteristics and turn-on voltage were more evident in the thick (1.2 µm) F8BT:EDA PLEDs. The neat F8BT device had both high current turn-on voltage (*V*_J) and luminance turn-on voltage (*V*_L) values of 20.0 and 19.8 V, whereas the F8BT:EDA device with the same thickness had much lower *V*_J and *V*_L values of 11.6 and 12.7 V, respectively (Figure 2c and Figure S6 and Table S1, Supporting Information).

To understand the relationship between device performance and thickness for the neat F8BT and F8BT:EDA devices, the corresponding $V_{\rm L}$ and $V_{\rm J}$ as a function of the thicknesses ranging from 60 nm to 1.2 μ m are summarized in Figure 2d and Figure S7





Figure 3. a) Transfer characteristics of F8BT OFETs ($L = 20 \,\mu$ m, $W = 2000 \,\mu$ m) on Si/SiO₂ (230 nm) with/without EDA. OFETs with EDA show an improved hole mobility from $1.6 \times 10^{-6} \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$ to $1.9 \times 10^{-5} \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$. b) *J*–V characteristics of hole-only neat F8BT and F8BT:EDA devices (100 nm). The hole mobility for F8BT:EDA is $2.2 \times 10^{-5} \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$. b) *J*–V characteristics of hole-only neat F8BT ($2.6 \times 10^{-8} \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$), which is three orders of magnitude higher than that of neat F8BT ($2.6 \times 10^{-8} \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$). c,d) HOMO energy levels and work function values for neat F8BT and F8BT:EDA films. The work function of F8BT increases by 110 meV by EDA and is constant during measurement, indicating stable p-type doping of F8BT by EDA. There is no change in F8BT HOMO level by EDA. The inset graph shows the F8BT energy levels, with the LUMO level calculated from the F8BT optical bandgap measured by its absorption.

in the Supporting Information. The F8BT:EDA active layers show a much reduced turn-on voltages compared to the neat F8BT devices (more details can be found in Figure S8, Supporting Information). The decrease in turn-on voltage in µm-thick devices implies that there is a significantly reduced hole injection barrier and improved hole/electron balance for the F8BT:EDA devices, which is essential for high-performance printable light-emitting applications. More importantly, the F8BT:EDA PLEDs with thin active layers (t < 200 nm) demonstrated reduced efficiency roll-off (Figure S9, Supporting Information). These results could provide further evidence that EDA doping in F8BT improves the devices by shifting the recombination zone away from a quenching interface.^[27] In addition, we found no differences in electroluminescence (EL) and current response times between neat F8BT and F8BT:EDA PLEDs, indicating no changes in transient behavior of devices included by EDA (Figure S10, Supporting Information). Therefore, we concluded that the small amount of EDA does not act as a luminance quencher in the active layer but plays an important role in improving the hole injection and charge balance of high-efficiency PLEDs.

4. Effects of EDAs on Hole Charge Injection and Balance in Devices

A field-effect transistor (FET) device configuration was used to compare hole transport in neat F8BT and F8BT:EDA (**Figure 3**a and Figure S11a, Supporting Information). Bottom-contact

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and bottom-gate F8BT or F8BT:EDA FETs were fabricated on heavily *n*-doped silicon/silicon oxide (SiO₂) ($t_{ox} = 230$ nm) with prepatterned Au source/drain electrodes (L = 2.5, 5, 10, and20 μ m and W = 2000 μ m). The neat F8BT FETs exhibited a very low hole charge carrier mobility ($\mu_{\rm h} = 1.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a negligible on/off ratio, which is likely caused by the large energy level offset between F8BT and the Au electrode (work function, $W_F \approx 5.1$ eV). In contrast the F8BT:EDA FETs showed an order of magnitude higher hole charge carrier mobility ($\mu_{\rm h} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). We evaluated the contact $(R_{\rm c}W)$ and channel resistance $(R_{\rm ch}/L)$ using the transfer line method (Figure S11b, Supporting Information). The $R_c W$ and $R_{\rm ch}/L$ of the neat F8BT FETs at $V_{\rm ds} = -2$ V and $V_{\rm gs} = -60$ V are 1.5×10^5 M Ω cm and 7.6×10^3 M Ω μ m⁻¹, respectively.^[28,29] The values of $R_c W$ and R_{ch}/L of the F8BT:EDA FETs at $V_{\rm ds}$ = -2 V and $V_{\rm gs}$ = -60 V were considerably lower at 7.0 imes 10^2 M Ω cm and 2.9×10^2 M Ω μ m⁻¹, respectively.

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While FET measurements allow evaluation of charge transport in the lateral direction, vertical charge injection and transport can be studied using hole-only (ITO/PEDOT:PSS/TFB/ active layer/MoO₃/Au) and electron-only (ITO/ZnO/active layer/Ca/Al) devices ($t_{active} \approx 100$ nm). There was little difference in current between the neat F8BT and F8BT:EDA blends in the electron-only devices, as electron injection is ohmic in both cases, and the impact of the EDA was less obvious (Figure S12, Supporting Information). However, for the hole-only devices, the hole current in the blends (F8BT:EDA) had a sharp turnon at 0.3 V and was approximately three orders of magnitude higher than that of neat F8BT (Figure 3b). We calculated the mobility from the space charge-limited current regime in the dark *J*–V curve obtained from the hole-only device using the following equation

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$
(1)

where $\varepsilon_{\rm r}$ is the relative dielectric constant of the polymer (typically \approx 3), ε_0 is the permittivity of free space, $\mu_{\rm h}$ is the hole mobility, *V* is the voltage drop across the device, and *L* is the semiconductor thickness.^[15] The hole mobility of neat F8BT is $\approx 2.6 \times 10^{-8} \, {\rm cm}^2 \, {\rm V}^{-1} \, {\rm s}^{-1}$, which is very similar to that obtained in a previous study (for $t_{\rm active} \approx 190 \, {\rm nm}$).^[15] while the hole mobility of F8BT:EDA was calculated to be $\approx 2.2 \times 10^{-5} \, {\rm cm}^2 \, {\rm V}^{-1} \, {\rm s}^{-1}$, which is three orders of magnitude higher than that of neat F8BT.

Based on the electrical measurements described above, we propose that under device operation the EDA reduces the hole injection barrier at the organic/electrode interface, which balances the charge carrier injection and mobility. This behavior is likely related to an interfacial EDA doping of F8BT, which changes the electronic structure of the interface. To study the interfacial doping and energetics of F8BT, we performed ambient photoemission spectroscopy (APS) and dark Kelvin probe measurements to evaluate the HOMO and work function of the neat F8BT and F8BT:EDA films (70 nm layers on top of an Au substrate (grounded)) (Figure 3c,d, respectively).^[30] A gold-plated probe tip with a diameter (*D*) of 2 mm was set close to the surface of samples to avoid electron–molecule scattering and thus obtain a desirable level of photoemission signal. The HOMO levels of both neat F8BT and F8BT:EDA are

measured to be \approx 5.8 eV, which is comparable to other experimental techniques, while the intensity of photoemission in F8BT:EDA was slightly lower than that in neat F8BT, which could be attributed to an electron-ion interaction. It is interesting to note that the work function of F8BT:EDA is \approx 110 meV higher than that of neat F8BT, indicating interfacial electrochemical doping of F8BT. This interfacial doping may make F8BT energetically more favorable for charge injection.

5. Modulation of the Energetics of Organic/ Electrode Interfaces via EDA-Induced Electrochemical Doping

We performed in situ electric-field dependent Raman spectroscopy for the neat and blend systems to directly monitor the impact of interfacial electrochemical doping on polymer conformation and hole injection during the device operation. The thickness of active layer, ≈150 nm was used to increase the range of voltages that can be applied. The Raman peaks of neat F8BT, 1314, 1357, 1425, 1457, 1486, 1545, and 1608 cm⁻¹, are well known and supported by our density functional theory (DFT) calculation at B3LYP 6.31G(d,p) (the details of the DFT calculations are provided in Figure S13, Supporting Information).^[31,32] When voltages between 0 and 7 V were applied to the neat F8BT PLEDs, there were no changes in the Raman spectra (Figure 4a). In contrast, for the F8BT:EDA devices, the Raman scattering intensity decreased as a function of the applied voltage (Figure 4b). The overall Raman intensity decreases due to the formation of (hole) polarons in F8BT, whose absorption is now nonresonant with the Raman excitation wavelength at 633 nm used, resulting in a decrease in the overall Raman intensities. When the Raman spectra obtained under different applied voltages are normalized to the C=C ring stretching mode of the F8 units (1608 cm⁻¹), the relative intensity of the particular Raman mode at 1457 cm⁻¹ (associated with F8 semicircular mode) exhibited a substantial increase (Figure 4c). This selective increase in the relative peak intensity at 1457 cm⁻¹ indicates specific electrochemical interaction occurring between the F8BT and EDA molecules under applied electric field. Such an electrochemical interaction increases π -electron density in F8 units (where HOMO is delocalized) providing a direct evidence of the electrochemical p-type doping of F8BT with the EDA molecules (Inset of Figure 4c).

Based on the results above, we propose that favorable charge injection and balance for PLEDs incorporating small quantities of EDA is achieved by the following mechanism (Figure 4d). In neat F8BT PLEDs, desirable hole injection and charge balance cannot be achieved due to the large energy level offset between the ITO/PEDOT:PSS/TFB layer and the neat F8BT layer. When a sufficient electric field is applied to F8BT:EDA PLEDs, F8BT and EDA start to interact leading to p-type doing of F8BT, which enables lowering the effective barrier for hole injection. This results in more effective hole injection and better charge balance, hence allowing charge recombination and emission to occur away from the quenching electrode interface, thereby significantly improving the device performance (i.e., turn-on voltage and efficiency roll-off effect), homogeneity and





Figure 4. a,b) In situ electric-field-dependent Raman spectra of neat F8BT and F8BT:EDA devices. c) Normalized and zoomed-in Raman spectra (inset) of an F8BT:EDA device (normalized to the 1608 cm⁻¹ peak), where the arrows indicate an increase in the Raman intensity of selected peaks (1457 cm⁻¹) under the electric field. d) The proposed mechanism for improved charge (hole) injection and charge balance in an F8BT:EDA device via electrochemical hole doping of F8BT by anion PF_6^- in EDA molecules (inset).

uniformity of the light-emitting properties of the corresponding PLEDs, which are critical parameters for facilitating printing technologies of large-area and high-performance PLEDs (Figure S14, Supporting Information).

6. Device Stability and the Degradation Mechanism of π -CPs:EDA PLEDs

The F8BT:EDA PLEDs show thickness-independent turn-on voltages and minimal efficiency roll-off, but device lifetime is also a critical factor in determining the suitability of PLED technologies for display applications.^[33,34] The stability and degradation mechanism of neat F8BT and F8BT:EDA PLEDs with $t_{active} = 100$ nm were investigated by monitoring the luminance (initial luminance of 1000 cd m⁻²) at a constant current as a function of operation time up to 7200 min in a nitrogen-filled chamber (**Figure 5**a). The neat devices had a half-life ($T_{1/2}$) of 1560 min and suffered from severe burn-in loss, but the blend devices demonstrated a 37% longer lifetime ($T_{1/2} = 2130$ min) and significantly less burn-in losses (inset of Figure 5a). The initial voltage stress at 1000 cd m⁻² of the neat F8BT PLEDs ($V_{ini} = 5.0$ V) was substantially higher than that of the F8BT:EDA PLEDs ($V_{ini} = 4.3$ V) due to the poor charge injection property

of the neat F8BT device (Figure 5b). After device operation for 7000 min, we found that the F8BT:EDA PLEDs showed a voltage increase of only 0.33 V to maintain a constant current, while the neat F8BT PLEDs exhibited a 0.56 V voltage increase. We consider that the reduction in burn-in loss in the F8BT:EDA PLEDs is mainly due to the relatively low voltage stress.

Figure 5c,d shows microscope images of the neat F8BT and F8BT:EDA PLED devices (area $\approx 3 \text{ mm}^2$), respectively, acquired after 120, 4000, and 7000 min. While both devices initially show no features, after 120 min of continuous operation, dark spots appear in the neat F8BT device. The generation of nonemissive dark spots in F8BT devices has been previously attributed to the dedoping of PEDOT:PSS due to pinholes or grain boundaries formed in the metal electrode during thermal evaporation.^[34] The number of dark spots increases as the devices remain subject to continuous voltage stress. The F8BT:EDA devices show only a few circularly shaped spots that remain unchanged throughout the 7000 min of operation. The improved operational lifetime and reduced degradation in F8BT:EDA PLEDs may be due to the lower operating voltage, which slows the evolution of dark spots, or the recombination zone, which is shifted away from the interface between PEDOT:PSS/TFB and F8BT in the presence of EDAs. This shift could prevent unwanted charge injection into and dedoping of the PEDOT:PSS layer.^[35]

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Figure 5. a,b) Normalized luminance and applied voltage during operation of neat F8BT (black line) and F8BT:EDA (red line) 100 nm thick devices with an initial luminance of 1000 cd m^{-2} . c,d) EL images of operating PLEDs without and with EDA at different operation times (120, 4000, and 7200 min). The red circle is a positional reference for comparing the sizes and numbers of black spots appearing in F8BT and F8BT:EDA devices during continuous operation.

7. Conclusions

In conclusion, we have successfully demonstrated that small quantities of an EDA can be used to improve the charge injection and balance for highly efficient and stable PLEDs. This improvement resulted from electrochemical doping of F8BT by EDA. For thin (<100 nm) F8BT:EDA PLEDs, we observed a negligible thickness-dependence on current and luminance turn-on voltages with reduced efficiency roll-off and operational driving voltage. A homogeneous emission in large-area devices was also achieved. For thick doped devices, a dramatic reduction in current and luminance turn-on voltages (7-8 V) was observed. The F8BT:EDA PLEDs also showed extended half-lifetime (from $T_{1/2} \approx 26$ to 35.5 h). Our study clearly demonstrates that by designing the EDA molecules with a long alkyl chain in its cation part and to form a solid state at room temperature, a favorable surface energy relative to π -CPs and an efficient and stable electrochemical doping can be achieved, which are critical for high-quality and efficient solution-processed PLEDs.

8. Experimental Section

Materials: F8BT was synthesized by Cambridge Display Technology (CDT), Inc., UK and was used as received. The average molecular weight of F8BT was 21 kg mol⁻¹. The EDA $[C_1C_{12}IM^+][PF_6^-]$ was synthesized through a conventional method described elsewhere. 1-Methylimidazole (99%), 1-bromododecane (97%), ammonium hexafluorophosphate

(99.99%), toluene, ethylacetate, and dichloromethane were purchased from Sigma-Aldrich. 1-Methylimidazole (6 g, 73.0 mmol) and 1-bromododecane (20 g, 80.2 mmol) were dissolved in dry toluene (80 mL). The mixture was stirred at 110 °C under nitrogen for 72 h. After the solvent was removed by rotary evaporation, the crude product was washed with cold ethyl acetate (-30 $^{\circ}\text{C},$ 100 mL), and 21.5 g of the white solid product was obtained with a yield of 89.0%. $[C_1C_{12}IM^+]$ [PF6⁻] (14.4 g, 43.4 mmol) was dissolved in deionized water (200 mL) and NH₄PF₆ (21.25 g, 130 mmol). The mixture was stirred at room temperature for 72 h. The generated solids were filtered and washed with water. After dissolving the solids in dichloromethane, MgSO₄ was then added to remove the moisture. The mixture solution was stored at a low temperature (-30 $^\circ$ C) for 24 h and filtered to remove MgSO₄ and the salt residue. After filtration, the filtrate was evacuated and vacuumed. A white solid, $[C_1C_{12}IM^+][PF_6^-]$ (16.2 g, 94.4%), was obtained. 1H NMR (400 MHz, dimethyl sulfoxide (DMSO)-d6) δ [ppm] = 0.83(3H, t), 1.24(18H, m), 1.72(2H, t), 3.84(3H, s), 4.07(2H, t), 7.69(1H, s), 7.76(1H, s), 9.09(1H, s). Electrospray ionization mass spectrometry (ESI-MS) (m/z) Positive ion: 251.2 [cation]⁺. Negative ion: 144.9 [anion]⁻.

Solution Preparation: Neat F8BT (for example, 15 mg) was directly dissolved in 1 mL of toluene to yield a concentration of 15 mg mL⁻¹. For the F8BT:EDA blend system, 0.075 mg of EDA was added to the neat F8BT solution. All solutions were stirred for 10 h in the dark and under ambient conditions.

UV-vis Absorption and Photoluminescence Spectroscopy and Thin Film Characterization: Quartz substrates were cleaned using acetone and isopropyl alcohol by sequential sonication for 5 min. F8BT or F8BT with EDA layers were spin coated on quartz substrates using the same solutions for both thin films and PLEDs. UV-vis absorption was measured using a Shimadzu UV-2550 UV-vis spectrophotometer. PL spectra were recorded in reflection geometry using a Jobin Yvon Horiba Fluoromax-3 spectrofluorometer

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of the thin films were determined using AFM (Park System). Device Fabrication and Characterization for PLED Applications: ITOpatterned glass substrates (size 12 mm \times 8 mm) were cleaned in an ultrasonic bath using acetone, isopropyl alcohol, and detergent (Hellmanex, 2% by volume in DI water) for 15 min, followed by washing in deionized (DI) water twice and baking at 115 °C for 10 min. After a 3 min UV-ozone treatment, a 40 nm thick PEDOT:PSS layer was spin coated onto the ITO substrate, which was then heated at 145 °C for 15 min. Then, a 15 nm thick hole-transporting and electron-blocking TFB interlayer was spin coated on top of the PEDOT:PSS layer and the assembly was baked under nitrogen at 180 °C for 1 h. Subsequently, an emissive layer of F8BT (Cambridge Display Technology, Ltd.) or F8BT with EDA was spin coated from a toluene solution. The thicknesses of the emissive layers were controlled by using different concentrations of solutions (12, 14.7, 16.2, 18, and 20.2 mg mL⁻¹ under 2000 rpm to form layers ranging from 60 to 112 nm; the error bar is 3 nm). Finally, calcium (25 nm) and aluminum (100 nm) cathodes were deposited via thermal evaporation under vacuum conditions (1×10^{-7} Torr). For hole-only and electron-only devices, neat F8BT and F8BT:EDA in 18 mg mL^{-1} solution were used to obtain 100 nm thick layers. The thicknesses of the MoO₃ and Au layers deposited by evaporation were 10 and 100 nm, respectively. ZnO with a 30 nm thickness on ITO was prepared from a 0.3 M zinc acetate dihydrate solution in 2-methoxyethanol and was annealed at 250 °C.

using an integrating sphere method. The surface roughness and morphology

For the PLED device measurements, the J-V-L characteristics and efficiencies of the PLEDs were measured using a Keithley 2400 source meter and a Minolta LS100 spot luminance meter under dark conditions. EL spectra were recorded using an Ocean Optics universal serial bus 2000 (USB 2000) charge-coupled device (CCD) spectrometer equipped with a fiber light collection bundle. All PLED measurements were carried out within a nitrogen-filled test chamber. Lifetime measurements were performed using the same experimental apparatus with an initial luminance (1000 cd m⁻²) at a constant current.

Device Fabrication and Characterization for Organic Field-Effect Transistor (OFET) Applications: To form gold bottom-gated and bottom-contacted devices, F8BT and F8BT:EDA OFETs were fabricated by spin-coating a 70 nm layer onto prepatterned SiO₂/Si wafer substrates (an insulating layer thickness of 230 nm) from the same solutions used in prepared the PLED devices. The OFET channel lengths (L) were 2.5, 5, 10, and 20 μ m, with a width W of 500 μ m. The output and transfer characteristics were recorded by an Agilent 4156C semiconductor parameter analyzer in a nitrogen-filled glovebox.

Measurements of APS and Kelvin Probe: The Kelvin probe (KP) technology APS-04 instrument was used to evaluate the energetics of neat F8BT and F8BT:EDA thin film. For APS measurements, the gold substrate-based sample was illuminated with UV light from a monochromatic deuterium lamp source (4–7 eV). KP WF measurements were taken by using a 2 mm gold alloy-coated vibrating tip above the surface of the sample. The resultant WF of the sample was calculated by the resulting contact potential difference between the tip and the sample added to the WF of the gold tip.

Measurements of In Situ Electric Field-Dependent Raman Spectroscopy: In situ Raman spectra of the PLED samples were collected using a specially designed chamber equipped with a probe station and Renishaw inVia Raman microscope (50X objective). Measurements taken with the excitation laser source at 633 nm were acquired at 0.5 mW using an acquisition time of 15 s when applying an external voltage from 0 to 7 V. A defocused laser beam with a diameter of ≈8 µm and flowing N₂ gas were used to avoid photodegradation of the samples. The obtained Raman spectra were background corrected by averaging the spectra obtained from three different regions of the samples. The spectra of the different regions are quite similar, confirming the reproducibility of the results.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge injection and balance, electrochemical doping, organic lightemitting diodes, organic semiconductors, solid-state ionic liquids

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