High-Efficiency Polymer LEDs with Fast Response Times Fabricated via Selection of Electron-Injecting Conjugated Polyelectrolyte Backbone Structure

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ABSTRACT

Imidazolium ionic side-group-containing fluorene-based conjugated polyelectrolytes (CPEs) with different π -conjugated structures, poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (F8im-Br) and poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene)-alt-(benzo(2,1,3)thiadiazol-4,8-diyl) dibromide (F8imBT-Br), are synthesized and utilized as an electron injection layer (EIL) in green-emitting F8BT polymer light-emitting diodes (PLEDs). Both CPE EIL devices significantly outperform Ca cathode devices; 17.9 cd A⁻¹ (at 3.8 V) and 16.6 lm W⁻¹ (at 3.0 V) for F8imBT-Br devices, 11.1 cd A⁻¹ (at 4.2 V) and 9.1 lm W⁻¹ (at 3.4 V) for F8im-Br devices, and 7.2 cd A⁻¹ (at 3.6 V) and 7.0 lm W⁻¹ (at 3.0 V) for Ca devices. Importantly, unlike the F8im-Br EIL devices, F8imBT-Br PLEDs exhibit much faster electroluminescence turn-on times (< 10 μ s) despite both EILs possessing the same tethered imidazolium and mobile bromide ions. The F8imBT-Br devices represent, to the best of our knowledge, the highest efficiency in thin (70 nm) single-layer F8BT PLEDs in conventional device architecture with the fastest EL response time using CPE EIL with mobile ions. Our results clearly indicate the importance of an additional factor of EIL materials, specifically the conjugated backbone structure, to determine the device efficiency and response times.

INTRODUCTION

Conjugated polyelectrolytes (CPEs) are a class of semiconducting polymers in which ionic functional groups are placed at the end of the solubilizing side-chain substituents attached to the main π -conjugated backbone. The incorporation of polar ionic groups enables CPEs to be soluble in alcohol/water-based polar solvents, which offers a wide range of applications including bio-related science.¹⁻³ In recent years, CPEs have been extensively studied in the field of organic optoelectronics as they can easily form a uniform thin film via solution processing on top of an emissive layer without suffering an intermixing problem between the two layers.⁴⁻¹⁰ It was reported that the charged nature of CPEs has the ability to enhance polymer light-emitting diode (PLED) efficiencies as a consequence of reduction in the energy barrier for electron injection from high work function metals, much in the same way that charge trapping can, but with greater control and no requirement for pre-stressing.¹¹ This is understood mainly due to the formation of permanent dipoles at the CPE/metal interface^{12, 13} as also achieved with dipolar self-assembled monolayers (SAMs), but without their need for specific interface chemistry.¹⁴ CPEs can also be used to improve the device performance of organic solar cells.¹⁵ As a consequence, the use of CPEs is regarded as a promising approach to realize high-performance printable organic electronics in a multilayer architecture using cost-effective solution processing techniques.

The advantageous features of CPE injection layers are, however, offset to a greater or lesser extent by electric-field-induced counter-ion rearrangements that can significantly increase the PLED current and luminance response times to of order a few seconds; too slow for video-rate display applications.^{16, 17} This situation is similar to the behaviour observed for PLEDs with deep charge traps.¹⁸ In an attempt to address such issues, Fang et al. fabricated PLEDs with

zwitterionic CPEs in which both anions and cations are covalently attached to the polymer side chains;¹⁹ the resulting PLED transient response was then ~1-100 μ s.

Here, we demonstrate high-performance green-emitting F8BT emission layer (EML) PLEDs using two different fluorene-based CPE electron injection layers (EILs) (Figure 1a) that have identical imidazolium ionic side groups but differ in their π -conjugated backbone structures. In one case a simple polyfluorene backbone is used (i.e. poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (F8im-Br)) and in the other a fluorene-benzothiadiazole alternating copolymer is used (i.e. poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene)-alt-(benzo(2,1,3)thiadiazol-4,8-diyl) dibromide) (F8imBT-Br)). We find that both F8imBT-Br and F8im-Br can significantly increase device efficiency relative to devices with conventional cathodes (Ca/Al). For example F8BT EML PLEDs with an F8imBT-Br EIL give 17.9 cd A⁻¹ at 3.8 V and 16.6 lm W⁻¹ at 3.0 V. However, unlike the F8im-Br EIL devices, F8imBT-Br PLEDs show much faster electroluminescence (EL) turn-on times (< 10 μ s). This is despite both EILs possessing the same tethered imidazolium and mobile bromide ions, and points to the importance of additional factors, specifically the energy level alignment between the EIL and emitter backbones.

RESULTS AND DISCUSSION

The PLED device architecture used is illustrated in Figure 1b. Both CPEs are readily dissolved in polar organic solvents, including 2-methoxyethanol, which do not dissolve conventional conjugated polymers (Figure S2 and Table S1). They are, consequently, readily deposited as EILs on top of the F8BT active layer prior to Al cathode evaporation. PLEDs with a 20 nm Ca cathode, capped with 100 nm of Al, were also prepared as reference devices.

First, to probe the interfacial energy levels in the F8BT/CPE/Al part of the device stack, we performed UV photoelectron spectroscopy (UPS) measurements on thin films of F8imBT-Br and F8im-Br (~10 nm) spin-coated on top of (~30 nm thickness) F8BT EMLs that had been spin-coated on ITO substrates (Figure S3). Based on UV-Vis absorption spectra the optical gap energies for F8imBT-Br and F8im-Br thin films were estimated to be 2.36 eV (526 nm) and 2.88 eV (431 nm), respectively (Figure S4). Combining these data with the UPS measurements allowed us to further estimate that the lowest unoccupied molecular orbital (LUMO) level of the F8imBT-Br EIL (4.07 eV) is well matched with the work function of the Al electrode (4.1 eV),²⁰ whereas that for F8im-Br is smaller (~3.84 eV) (Table S2). The corresponding energy barriers for electron injection from the Al electrode are then expected to be ~ 0.03 eV for F8imBT-Br and ~ 0.26 eV for F8im-Br, respectively.

Figure 2a shows the current density-voltage-luminance (*J-V-L*) characteristics of the F8BT EML PLEDs with different EILs. The thickness of the EILs was ~10 nm for both CPE materials. AFM images of F8imBT-Br and F8im-Br layers on ITO substrates confirm that both CPE thin films display uniform morphology without visible defects (Figure S5). The contact angle measurements also confirm a full uniform coverage of the CPE layer on top of the F8BT EML (Figure S6). The current density above the threshold is about 5 times greater for the Ca/Al device than for the CPE devices. Given the evidence from the efficiency data (see below) this is likely due to excess electrons travelling through the F8BT EML without generating excitons; Ca has a work function of 2.9 eV and is known to form an ohmic contact with F8BT.²¹ We also note that the deduced (from the UPS analysis) lower electron injection barrier for F8imBT-Br compared with F8im-Br is consistent with the higher current density observed at low drive voltages (< 3.5 V) for the F8imBT-Br/Al device compared with the F8im-Br/Al device.

To gain deeper insight into the role of CPE EIL layers, in particular for hole-blocking and electron-injecting properties, we have fabricated and measured hole-only and electron-only F8BT devices (Figure S7). We observe that hole-only devices with CPE EIL layers show much lower (almost one order of magnitude lower) current density than Au device ($< 4\text{V}$), clearly showing good hole-blocking property of CPE layers. On the other hand, there is a significant increase in the current density for electron-only devices with CPE EILs compared to Al device. The current density of F8imBT-Br CPE EIL device is almost three orders of magnitude higher than that of Al device. Based on these single carrier device results, we consider that the high leakage current $< 2\text{V}$ observed in bipolar F8BT PLEDs with CPE EILs is due to excess electron current. Finally, both of the CPE EIL devices produce higher luminance at a given current density than the Ca/Al device (see inset to Figure 2a). The F8imBT-Br/Al device gives $15,800\text{ cd m}^{-2}$ at 100 mA cm^{-2} , 1.4 times higher than the F8im-Br/Al ($11,030\text{ cd m}^{-2}$) device and 2.2 times the Ca/Al ($7,160\text{ cd m}^{-2}$) device.

Figure 2b presents the luminous and luminous power efficiencies as a function of voltage for the same F8BT PLEDs. The performance of the three devices is summarized in Table 1. Overall, the CPE EIL devices show higher device efficiencies than the Ca/Al device with increasing luminance. The F8im-Br/Al device degrades quicker than the Ca/Al devices above $\sim 26,000\text{ cd m}^{-2}$. Interestingly, the F8imBT-Br/Al device performs better than the other two devices; a luminous efficiency of 10.8 cd A^{-1} and a luminous power efficiency of 14.3 lm W^{-1} at 100 cd m^{-2} , rising up to 15.5 cd A^{-1} and 16.5 lm W^{-1} at $1,000\text{ cd m}^{-2}$. The efficiency values at 100 cd m^{-2} are 6.2 cd A^{-1} and 7.0 lm W^{-1} for the F8im-Br/Al device and 3.9 cd A^{-1} and 5.0 lm W^{-1} for the Ca/Al device, respectively. These values increase at $1,000\text{ cd m}^{-2}$ to 9.4 cd A^{-1} and 9.1 lm W^{-1} for the F8im-Br/Al device and 6.0 cd A^{-1} and 6.7 lm W^{-1} for the Ca/Al device, respectively. The

significantly higher efficiencies for the CPE/Al devices compared to the Ca/Al device suggest that the electron and hole densities within their F8BT EMLs are better balanced. Note that in all devices tested here, hole injection (and device stability) is optimized by inclusion of a thin TFB interlayer between the PEDOT:PSS coated ITO anode and the F8BT EML.²²⁻²⁴

Figure 2c shows normalized EL spectra of the CPE/Al and Ca/Al devices that suggest that the emission predominantly originates from the F8BT EML.²⁵ The corresponding photoluminescence (PL) spectra of F8imBT-Br and F8im-Br thin films are distinct from those shown in Figure 2c, peaking at 575 nm for F8imBT-Br and 430 nm for F8im-Br (Figure S4). The fact that the EL spectra of the F8imBT-Br and F8im-Br CPE devices are, nevertheless, identical confirms that the CPE layers do not contribute to the EL emission. The slight reduction in EL at longer wavelengths (550 to 700 nm) compared to Ca/Al devices suggests that the electron-hole recombination zone within the CPE devices has a different spatial distribution across the F8BT EML thereby modifying the expected weak cavity effect contributions to the spectral distribution.^{26, 27} Another factor to consider is that, in the presence of heterogeneity within the EML, shifting the recombination zone will sample different ensembles of chains and these will tend to emit at different energies.²⁸

The traces in Figures 3a and b show the normalized transient response curves for current density (J) and EL intensity for the three PLED types. These were measured with 4 V amplitude, 1 Hz repetition rate, and square wave pulses. The J and EL signals for the Ca/Al devices closely follow the square wave pulses. For the F8im-Br/Al devices, following an initial $\sim 50\%$ rapid step in magnitude, there is a more gradual increase in J and EL intensity with time constant ~ 0.25 seconds, as also previously reported for other CPE EILs containing potentially mobile counter-ions.¹⁶ In contrast, the F8imBT-Br/Al devices display a much faster ($<10\ \mu\text{s}$) rise in J

and EL to their peak values followed by a slow decrease ($\sim 5\%$ drop during the 0.5s pulse width). There is, however, no accumulated decay in EL intensity from one pulse to the next indicating that the devices do not undergo irreversible degradation. We observed that the EL transient response of the F8imBT-Br/Al devices with different F8imBT-Br film thicknesses (from 5 to 10 nm) is overlapped each other (Figure S8). The un-normalized EL intensities of the three devices are plotted as a function of time on a log scale in Figure 3c. The F8im-Br/Al device shows a distinct short time (small magnitude) peak followed by a gradual rise. The F8imBT-Br/Al device behaves more like a Ca/Al device. The EL signal rises quickly to its peak value but unlike the Ca/Al device then slowly decays by 5 %. The initial spike seen for the EL transient in F8im-Br/Al devices has been observed for other PLEDs with polyelectrolyte EILs and is generally attributed to ion rearrangement under the applied electric field.^{19, 29}

The delay (t_d) and rise time (t_r) values (see Figure S9) for the appearance and growth in PLED EL intensity for different EIL devices are summarized in Table 1. The delay time is the time between the on-set of the voltage pulse and the initial rise in EL signal (estimated from the intercept between tangents to the rising EL slope and the EL baseline). This represents the time taken for electrons and holes to combine and produce a measurable radiative output.³⁰ The rise time is defined as the time between the on-set of the voltage pulse and an asymptote to the rising edge of the EL reaching the EL maximum value. This represents the time beyond which the EL tends to saturate. It reflects the build-up time for the minority carrier density in the recombination zone³⁰ (Figure S9). In the case of the F8im-Br/Al device, the initial spike in the EL is disregarded for the purpose of determining the rise time. The F8imBT-Br/Al and Ca/Al devices have similar rise times (5.15 μs and 3.94 μs respectively) that are much shorter than for

F8im-Br/Al devices ($\sim 10^5$ μ s). Delay times are more similar, being < 500 ns for all three devices and more or less identical for the Ca/Al and F8im-Br/Al devices.

The F8imBT-Br/Al rise time represents, to the best of our knowledge, the fastest EL response for PLEDs using CPE EILs with mobile ions. In a series of earlier reports it has been shown that the transient response of mobile ion possessing CPE-based PLEDs is strongly dependent on the ion size and environment (including neighboring functional groups).^{9, 12, 13, 19, 29, 31} The striking difference here between F8im-Br and F8imBT-Br which possess the same mobile bromide ion and imidazolium side chain tethered ionic groups represents a significant deviation from typical behavior. The low electron injection barrier for F8imBT-Br in contact with the Al electrode might also contribute to the fast transient response observed by minimizing the field dropped across the EIL. However, one recent study suggested that the response time is controlled by molecular reorientation within the thin CPE layer rather than ion migration under the influence of the applied bias field.³² In the latter scenario the difference in CPE π -conjugated backbone structure may lead to differences in ordering and flexibility through specific anion- π interactions involving the electron deficient BT unit.³³

Another yellow light-emitting polymer (SY-PPV) is characterized for PLEDs with F8imBT-Br EIL and compared to Ca/Al devices (Figure S10). Note that SY-PPV is a hole-dominated polymer and has a different π -conjugated backbone structure compared to F8imBT-Br CPE producing different LUMO energy levels; 2.7 eV for SY-PPV³⁵ and 4.07 eV for F8imBT-Br. The fast EL rise time (~ 12 μ s) with F8imBT-Br CPE layer, comparable to that of F8BT devices (< 10 μ s with F8imBT-Br CPE), is also observed for SY-PPV devices (Figure S11). However, SY-PPV devices show much poorer device efficiencies with this CPE EIL (0.58 cd A⁻¹ and 0.28 lm W⁻¹ for F8imBT-Br) compared to Ca/Al devices (6.0 cd A⁻¹ and 2.8 lm W⁻¹). These results

confirm our main conclusion that the π -conjugated backbone of CPE materials plays an important role in achieving both fast response time and high efficiency of PLEDs, even with the presence of the mobile ions in CPE.

CONCLUSIONS

In conclusion, we have successfully demonstrated high-performance green-emitting F8BT PLEDs with CPE EILs comprising different π -conjugated backbone structures (F8imBT-Br and F8im-Br). Both CPE EIL devices outperform Ca cathode devices in respect of luminous and luminous power efficiencies. The F8imBT-Br/Al device shows 10.8 cd A⁻¹ and 14.3 lm W⁻¹ at 100 cd m⁻² and 15.5 cd A⁻¹ and 16.5 lm W⁻¹ at 1,000 cd m⁻². The efficiency peaks are 17.9 cd A⁻¹ and 16.6 lm W⁻¹, which are significantly higher than the devices with F8im-Br EIL (11.1 cd A⁻¹ and 9.1 lm W⁻¹) and Ca EIL (7.2 cd A⁻¹ and 7.0 lm W⁻¹). The substitution of a strong electron withdrawing group (BT, benzothiadiazole) in the π -conjugated backbone structure of the CPE, namely F8imBT-Br, not only allows the lowering of the electron injection barrier at the EML/CPE interface but also leads to a fast transient EL response in the microsecond time scale ($t_r = 5.15 \mu\text{s}$) despite the presence of potentially mobile ions. Our results show that it is not only the tethered ionic side groups and mobile ions in CPEs that are important for PLED efficiency and response time but that the CPE π -conjugated backbone structure also plays a crucial role. Further detailed investigations probing this effect are underway. Finally, the same principles should apply to optimizing the emission efficiency of PLEDs containing green poly(phenylenevinylene) EMLs³⁴ that have HOMO and LUMO energy levels close to those of F8BT.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental methods including material synthesis and ^1H NMR and additional figures (Figure S1-S11) are available. The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

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MS and JB contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

CPE, conjugated polyelectrolytes; PLED, polymer light-emitting diode; EML, emission layer; EIL, electron injection layer; UPS, UV photoelectron spectroscopy; EL, electroluminescence; PL, photoluminescence; LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital.

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(a)

(b)

Figure 1. (a) Chemical structures of F8imBT-Br and F8im-Br. (b) Device configuration of F8BT EML PLED and corresponding energy level diagram (in eV).

Figure 2. (a) J - V - L characteristics of F8BT PLEDs with F8imBT-Br and F8im-Br EILs; filled symbols are J , open symbols are L . Data for Ca/Al devices is also shown for comparison. Inset: L - J curves for all three devices. (b) Luminous (cd A^{-1}) and luminous power (lm W^{-1}) efficiencies as a function of voltage for the F8BT PLEDs. (c) Normalized EL spectra of the F8BT PLEDs at 4.5 V.

Figure 3. Normalized transient response for the (a) J and (b) EL intensity of F8BT PLEDs with F8imBT-Br and F8im-Br EILs. Data for Ca/Al devices is also shown for comparison. (c) Non-normalised EL transient responses for all three PLEDs plotted on a log scale. Data were obtained using 1 Hz repetition rate, 4.0 V amplitude, square pulses.

Table 1. Performance parameters for F8BT EML PLEDs with F8imBT-Br and F8im-Br EILs. The results for equivalent Ca cathode devices are also shown for comparison.

Cathode	Luminous Efficiency, η_L (cd/A)			Luminous Power Efficiency, η_P (lm/W)			Maximum EQE	t_d (ns)	t_r (μ s)
	Peak	@ 100 cd/m ²	@ 1000 cd/m ²	Peak	@ 100 cd/m ²	@ 1000 cd/m ²	(%)		
Ca/Al	7.2 @ 3.6 V	3.9	6.0	7.0 @ 3.0 V	5.0	6.7	2.1 @ 9,943 cd/m ²	393	3.94
F8imBT-Br/Al	17.9 @ 3.8 V	10.8	15.5	16.6 @ 3.0 V	14.3	16.5	5.1 @ 5,089 cd/m ²	490	5.15
F8im-Br/Al	11.1 @ 4.2 V	6.2	9.4	9.1 @ 3.4 V	7.0	9.1	3.1 @ 7,275 cd/m ²	391	$\sim 10^5$

Table of Contents

Supporting Information

High-Efficiency Polymer LEDs with Fast Response Times Fabricated via Selection of Electron-Injecting Conjugated Polyelectrolyte Backbone Structure

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Synthesis of CPEs

All chemical reagents were obtained from Aldrich and used as received. Nuclear magnetic resonance (^1H NMR) spectra were collected on a JEOL JNM-AL400 spectrometer at 400 MHz. The ^1H NMR data were recorded in CDCl_3 (δ 7.26 ppm) and CD_3OD (δ 3.31 ppm) as internal standards. Molecular weights of the polymer were determined by gel permeation chromatography (GPC) analysis on a Waters Breeze HPLC instrument, using tetrahydrofuran (THF) as an eluent and a calibration curve of polystyrene standards. F8im-Br CPE was prepared by the method described in the literature.^{S1}

2,7-dibromo-9,9-bis(8'-bromooctyl)fluorene (M1). 2,7-dibromofluorene (5 g, 15.4 mmol), 1,8-dibromooctane (13.82 g, 50.8 mmol), and tetrabutylammonium bromide (0.5 g, 1.54 mmol) were dissolved in THF (40 ml) at room temperature under inert atmosphere. To the mixture, KOH aqueous solution (16 ml) was added dropwise. The reaction mixture was allowed to stir at 70 °C for 6 h and then was diluted with water. The solution was extracted with THF, and the combined organic layer was dried over MgSO_4 , filtered, and concentrated by rotary evaporator. The obtained product was purified by column chromatography (silica gel, hexane) to afford M1 (4.5 g, 41 %) as a white powder. ^1H NMR (400 MHz, CDCl_3 , TMS), $\delta(\text{ppm})$ = 7.53 - 7.44 (m, 6 H; Ar-H), 3.34 (t, $J=8$ Hz, 4 H; $-\text{CH}_2$), 1.94 - 1.90 (m, 4 H; $-\text{CH}_2$), 1.79 - 1.72 (m, 4 H; $-\text{CH}_2$), 1.33 - 1.24 (m, 4 H; $-\text{CH}_2$), 1.17 - 0.99 (m, 12 H; $-\text{CH}_2$), 0.63 - 0.52 (m, 4 H; $-\text{CH}_2$).

Figure S1. ^1H NMR spectrum of the monomer M1.

General procedure for polymerization. Polymerizations were carried out using palladium-catalyzed Suzuki coupling reaction. Equivalent molar ratios of a diboronic acid ester monomer and a dibromo monomer (M1), and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) (0.2-1.0 mol % with respect to the monomer) were dissolved in a mixture of toluene and aqueous 2 M K_3PO_4 . The reaction mixture was refluxed with vigorous stirring for 36 h under nitrogen atmosphere. After the solution was cooled to room temperature, it was poured into methanol. The precipitate was collected by filtration and was washed with acetone. The precipitate dissolved in dichloromethane was further washed with aqueous 2 M HCl to remove any terminal

boronates on the polymer chain. Then, the organic layer was separated, dried over MgSO_4 , and concentrated under reduced pressure to yield a crude solid. The solid was redissolved in a minimal amount of chloroform and added to methanol, giving a precipitate. The resulting precipitate was recovered by filtration and washed successively for 48 h using acetone to remove residual impurities. It was then dried overnight in vacuum at 60 °C. **Poly[(9,9-bis(8'-bromooctyl))-2,7-fluorene)-*alt*-(benzo(2,1,3)thiadiazol-4,8-diyl)] (F8BT-Br)**. M1 (1.41 g, 2 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.78 g, 2mmol), and $\text{Pd(PPh}_3)_4$ (4 mg) in a mixture of toluene (20 ml) and aqueous 2 M Na_2CO_3 (10 ml) were degassed and stirred at 80 °C for 36 h. The desired polymer was precipitated, washed, and dried in vacuum to afford F8BT-Br (1.8 g, 63 %) as an orange powder. ^1H NMR (400 MHz, CDCl_3 , TMS), $\delta(\text{ppm})$ = 8.18 - 7.45 (m, 8 H; Ar-H), 3.35 (m, 4 H; $-\text{CH}_2$), 2.16 (m, 4 H; $-\text{CH}_2$), 1.78 - 1.73 (m, 4 H; $-\text{CH}_2$), 1.32 (m, 4 H; $-\text{CH}_2$) 1.17 (m, 12 H; $-\text{CH}_2$), 0.97 - 0.81 ppm (m, 4 H; $-\text{CH}_2$). GPC: M_n = 4,790 g mol^{-1} , M_w = 9,916 g mol^{-1} , PDI = 2.01.

General procedure for imidazolium substitution reaction. The precursor polymer and 1-methylimidazole in the ratio of 1:30 by weight were dissolved in toluene at room temperature under nitrogen atmosphere. Upon complete dissolution, the reaction mixture was heated to reflux for 4 h and the precipitate was dissolved by adding methanol. Stirring was subsequently continued for 48 h. After the solution was cooled to room temperature, it was poured into acetone to precipitate the desired polymer. The resulting polymer was recovered by filtration, washed with acetone, and dried overnight in vacuum to obtain the final polymer with the imidazolium substitution. Yield: ~70 %. **Poly[(9,9-bis(8'-(3"-methyl-1"-imidazolium)octyl))-2,7-fluorene)-*alt*-(benzo(2,1,3)thiadiazol-4,8-diyl)] dibromide (F8imBT-Br)**. The polymer

was derived from F8BT-Br by the reaction procedure mentioned above. ^1H NMR (400 MHz, CD_3OD , TMS), $\delta(\text{ppm}) = 8.80$ (br, 2 H, Ar-H), 8.24 - 7.40 (br, 10 H; Ar-H), 4.12 (br, 4 H; $-\text{CH}_2$), 3.88 (br, 6 H; $-\text{CH}_3$), 2.26 - 2.16 (br, 4 H; $-\text{CH}_2$), 1.76 (br, 6 H; $-\text{CH}_2$), 1.17 (br, 12 H; $-\text{CH}_2$), 0.84 (m, 6 H; $-\text{CH}_2$).

PLED fabrication: ITO patterned glass substrates were ultrasonicated in methanol, acetone, and isopropyl alcohol and then dried in an oven at 120 °C. The substrates were then oxygen plasma treated prior to spin-coating of the polymer solutions.^{S2} A 40-nm-thickness PEDOT:PSS (poly(ethylenedioxythiophene):poly(styrenesulfonate), Baytron P AI4083) layer was spin-coated as a hole injection layer onto an ITO coated glass substrate, followed by annealing at 150 °C for 30 min. A solution of TFB (poly(2,7-(9,9-di-n-octylfluorene)-*alt*-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)) in *p*-xylene was spin-coated to form a 10~15-nm-thickness film and annealed at 180 °C for 1 h in a nitrogen atmosphere. Subsequently, a 70-nm-thickness F8BT (poly((9,9-di-n-octylfluorenyl-2,7-diyl)-*alt*-(benzo(2,1,3)thiadiazol-4,8-diyl)) emissive layer was spin-coated from a 10 mg ml^{-1} *p*-xylene solution. A thin layer of the CPE was then spin-coated on top from a 2 mg ml^{-1} 2-methoxyethanol solution without any subsequent post-annealing step. Finally, a 120-nm-thick Al metal layer was thermally evaporated inside a vacuum chamber (1×10^{-7} Torr). All fabrication procedures except the substrate cleaning were performed inside a glove box under nitrogen atmosphere.

Device characterization: The *J-V-L* characteristics of the PLEDs were recorded using a Keithley 2635A source meter interfaced with a Minolta CS2000 spectrophotometer in a dark box. The efficiencies were calculated from this data using the standard protocols.^{S3} The PLED EL intensity and current density transient responses were probed using a HP 3325B pulse generator

and monitored with a digital oscilloscope (Tektronix DPO 3054); a fast Si-photodiode was used to detect the EL signal. All measurements were carried out within a nitrogen-filled test chamber.

Thin film characterization: The morphology of the polymer thin films was assessed using a PSIA XE-100 scanning probe microscope (Park Systems) in tapping mode. PL and UV-Vis spectra were recorded using Hitachi F-7000 and Shimadzu UV-3101PC spectrophotometers, respectively. UPS measurements were carried out *in vacuo* (1×10^{-10} Torr) with a PHI Versaprobe XPS system equipped with a UV source (He II at 40.8 eV) and hemispherical energy analyzer.

Figure S2. Photographic images of F8imBT-Br mixed with various solvents. Left imaged in daylight and right in the dark with 365 nm UV-excitation. MC refers to methyl cellosolve (2-methoxyethanol). The colouration of the solvents and corresponding fluorescence under UV-excitation demonstrates good solubility.

Table S1. Solubility of F8imBT-Br and the precursor polymer F8BT-Br. ‘x’ denotes insoluble and ‘o’ soluble.

	H ₂ O	MeOH	MC	THF	Toluene
F8BT-Br (precursor polymer)	×	×	×	○	○
F8imBT-Br	×	○	○	×	×

F8imBT-Br has good solubility in polar organic solvents while the precursor polymer F8BT-Br only dissolves in non-polar organic solvents (as is also the case for many other conventional conjugated polymers).

Figure S3. UPS spectra of F8BT and F8BT/CPE thin films; (a) secondary electron region, (b) valence band region and (c) the photoemission onset in greater detail.

Figure S4. Normalized UV-Vis (dashed) and PL (solid) spectra of F8imBT-Br and F8im-Br thin films on quartz.

Table S2. Energy level data for CPE thin films on top of F8BT

	UV-Vis absorption		UPS		E_{LUMO} (eV)
	Optical onset (nm)	Optical gap (eV)	Valence band onset	E_{HOMO}	
F8BT	-	2.4 ^{S4}	1.43	6.06	3.66
F8im-Br	431	2.88	2.12	6.72	3.84
F8imBT-Br	526	2.36	1.83	6.43	4.07

The optical gap energy (E_g) is estimated from the UV-Vis absorption spectra in Figure S4.

The HOMO energy is estimated from the UPS spectra in Figure S3. The work function value of the ITO electrode is estimated to be 4.6 eV from the UPS data and the LUMO energy of the CPEs is estimated by subtracting the optical gap energy from the HOMO energy.

Figure S5. AFM images of thin films (10 nm) of F8imBT-Br (left) and F8im-Br (right) spin-coated on ITO substrates. The scan size is 10 x 10 μm .

Figure S6. Surface angle measurements with (left) and without (right) F8imBT-Br CPE layer on top of F8BT film.

Figure S7. Current density of (a) electron-only and (b) hole-only devices with different CPE EILs.

Figure S8. Normalized EL transient response of F8BT PLEDs with different film thicknesses of F8imBT-Br EIL at a frequency of 1 Hz for amplitude of 4.0 V.

Figure S9. EL transient measurement data for F8BT PLEDs with CPE EILs. The procedures for determining the rise (t_r) and delay times (t_d) (inset) are illustrated.

Figure S10. Device characteristics of SY-PPV PLEDs with F8imBT-Br EIL; (a) J-V-L, (b) luminous and (c) power efficiencies as a function of applied voltage. The device structure; ITO/PEDOT/TFB/SY-PPV/EIL/Al.

Figure S11. Normalized EL transient response of SY-PPV PLEDs with F8imBT-Br EIL at a frequency of 1 Hz for amplitude of 7.0 V. The inset shows how the rise time (t_r) is determined.

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