

Ionic Density Control of Conjugated Polyelectrolytes via Postpolymerization Modification to Enhance Hole-Blocking Property for Highly Efficient PLEDs with Fast Response Times

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For an ideal electron interlayer, both electron injection and hole-blocking properties are important to achieve better polymer light-emitting devices (PLEDs) performance. Conjugated polyelectrolytes (CPEs) are applied widely in PLEDs to enhance charge injection. Understanding the role of backbone structures and energetic matching between the CPEs and emitters can benefit charge injection and balance. Herein, a postpolymerization approach to introduce varying amounts of alkyl sulfonate groups onto the backbone of a copolymer of 5-fluoro-2,1,3-benzothiadiazole and 9,9'-dioctylfluorene is utilized. This study finds that device performance is dependent on the percentage of sulfonate groups incorporated, with the optimal copolymer (CPE-50%) maintaining efficient ohmic electron injection and gaining enhanced hole-blocking properties, thereby achieving the most balanced hole/electron current. Therefore, the PLED with CPE-50% interlayer exhibits the highest efficiency (20.3 cd A^{-1} , 20.2 lm W^{-1}) and the fastest response time ($4.3 \mu\text{s}$), which is the highest efficiency among conventional thin (70 nm) F8BT PLEDs with CPEs. These results highlight the importance of balanced charge carrier density in CPEs and highlight that postpolymerization modification is a useful method for fine-tuning ionic content.

1. Introduction

Conjugated polyelectrolytes (CPEs) have attracted considerable attention due to their promising application potential in organic optoelectronic devices, chemo-/biosensors, and cell imaging.^[1–3] CPEs are polymers consisting of backbones with π -delocalized electronic structures and side chains containing ionic groups (such as phosphate, carboxyl, quaternary ammonium, anionic carboxyl, sulfonic, and zwitterionic groups).^[1,2,4] The ionic nature of the side chains enables CPEs to be soluble in polar solvents, which makes CPEs perfect as interfacial materials to fabricate multilayered organic electronic devices such as polymer light-emitting diodes (PLEDs) and organic (or perovskite) photovoltaic cells (OPVs).^[2,5–7] Substantial efforts have been made to develop new CPE interlayer materials to fulfill versatile applications in organic electronics. For example, many types of highly polar pendant groups

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DOI: 10.1002/adom.202300988

(such as cationic, anionic, zwitterionic, and neutral highly polar pendant groups) and novel building blocks (such as fluorene, carbazole, triphenylamine, and thiophene) have been used to develop CPEs as interfacial layers.^[2] There are several demonstrated mechanisms for charge injection by conjugated polyelectrolytes. For thin (<10 nm) CPE layers, the formation of permanent dipoles at the CPE/metal interface can lower the energy barrier for electron injection, thereby increasing PLED efficiencies.^[1,8–10] However, for thick CPE layers (20–30 nm), ion rearrangement and electric field screening together with interfacial charge accumulation can redistribute the internal field to enable efficient electron injection via the formation of tunneling junctions.^[11,12] Song and co-workers demonstrated that the permanent dipole model is suitable for 2 nm thick CPEs, while the ion migration model can be applied for even 10 nm thick CPEs. These proposed mechanisms highlight the importance of ionic groups, molecular orientation, and dipole directions.

It has been previously reported that CPEs with different backbone structures can also strongly influence CPE-LED performance by controlling the charge injection barrier. Recently, some of us reported a high-performance green-emitting F8BT PLED with CPE electron injection layers (EILs) comprising different π -conjugated backbone structures (F8imBT-Br and F8im-Br).^[13,14] The F8imBT-Br/Al device displayed high device efficiencies of 17.9 cd A⁻¹ and 16.6 lm W⁻¹. This improvement was attributed to the lower electron injection barrier between F8imBT-Br CPE and Al (0.03 eV).^[13] However, the LUMO mismatch between F8BT and F8imBT-Br CPE ($\Delta E = 0.41$ eV) was larger than that between F8BT and F8im-Br CPE ($\Delta E = 0.18$ eV). Lee and co-workers investigated the performance of MEH-PPV PLEDs with a series of CPEs of varying ionic density. They found that PLED performance did not increase linearly with ionic density.^[8] Similarly, in 2018, Song and co-workers investigated a range of CPEs with differing amounts of ionic side chains. They found that a combination of ionic density and electric poling (positive or negative) could be used to modulate the interfacial energy level and hence charge injection/extraction.^[12] These studies highlight the importance of the elimination of electron injection barriers by controlling the polymer backbone and ionic density of CPEs. However, a complication arises in terms of the different molecular weight and polydispersity for the various CPE copolymers reported, which varied along with ionic density, making it difficult to disentangle the effect of molecular weight and polydispersity of CPE copolymers on device performance. Furthermore, there was little investigation into how backbone modification and ionic density can influence charge carrier balance.

Balanced hole/electron current in PLEDs can shift the recombination zones away from material interfaces and prevent exciton quenching.^[15,16] Kim et al. reported that adding a thin TFB interlayer between PEDOT:PSS and emitter can significantly improve device efficiency, as this TFB interlayer can act as an efficient exciton-blocking layer.^[17] In 2018, Friend et al. also reported the importance of electron blocking by changing CPE backbones as hole injection layers in perovskite LEDs.^[5] Therefore, for electron-dominant devices, instead of enhancing electron injection, improving the hole-blocking property of CPEs by modulating their chemical structures is expected to be more

important.^[13,18] Therefore, understanding the effect of backbone structures and energy alignment between CPEs and emitters will be of direct benefit to PLED device improvement.

Finding an effective method to control precisely the ionic density and molecular structures, and hence the energetics of CPEs remains a significant challenge, severely restricting the understanding of structure–property correlations and material applications of CPEs. Here, we synthesized a series of CPEs with different ratios of ionic side groups and fluorinated BT (FBT) units by a postpolymerization modification method aiming to precisely control the energy levels and ionic densities.^[19] This methodology utilizes reactions on the backbone of poly(9,9'-dioctylfluorene-co-5-fluoro-2,1,3-benzothiadiazole) (F8FBT) in which fluorine is selectively substituted by a thiol-containing ionic sulfonate group. Since a single batch of F8FBT was used for all functionalization, a series of CPEs with consistent polymer repeat length and dispersity is produced, avoiding the issues with molecular weight variation that often come from random copolymerizations.^[20] We find that all the CPEs can significantly increase device efficiency relative to devices with only conventional cathodes (Ca/Al). Thus a device incorporating a CPE with 50% functionalization (CPE-50%), together with the emissive polymer F8BT gives 20.3 cd A⁻¹ at 5.8 V and 20.2 lm W⁻¹ at 2.4 V, which is state of art for thin (70 nm) F8BT conventional PLEDs with CPE. By calculating the energy level of CPEs obtained from ambient photoemission spectroscopy (APS) and optical absorption spectroscopy, the electron injection barrier from the CPE to F8BT is minimal ensuring efficient electron injection and fast response times. In addition, by conducting work function (WF) and single carrier limited current (SCLC) measurement, we find that the CPE-50% device has the best hole-blocking properties, leading to superior charge carrier balance than its two analogues. Therefore, we demonstrate a new postpolymerization approach to precisely control ionic density and energy levels for developing efficient CPE-LEDs.

2. Results and discussion

F8FBT was synthesized as previously reported with a weight average molecular weight (M_w) of 67,500 g mol⁻¹ as measured by gel permeation chromatography against polystyrene standards.^[19] The ionic groups were introduced by a reaction of the readily available sodium 3-mercapto-1-propanesulfonate in the presence of sodium hydroxide in a mixed solvent of chlorobenzene and DMSO. The ionic density on the backbone was controlled by varying the relative amount of the nucleophile present to give conjugated polyelectrolytes with three different densities of ionic groups, CPE-50%, CPE-75%, and CPE-100% (see **Figure 1a**). The successful synthesis of CPEs was confirmed by high-temperature ¹H NMR. Specifically, for CPE 100%, the synthesis characterization was also confirmed by the disappearance of fluorine signal from ¹⁹F NMR. It was further verified using X-ray photoelectron spectroscopy (XPS) analysis. The absence of the C–F peak in C 1s core-level spectra for CPE 100% confirmed the complete replacement of fluorine with ionic group. As the density of ionic side chain increased, the intensity of SO₃⁻ and C–S–C peak in S 2p core level also gradually increased (see **Figure 2** and **Figure S9**, Supporting Information). The detailed atomic composition of CPEs calculated from

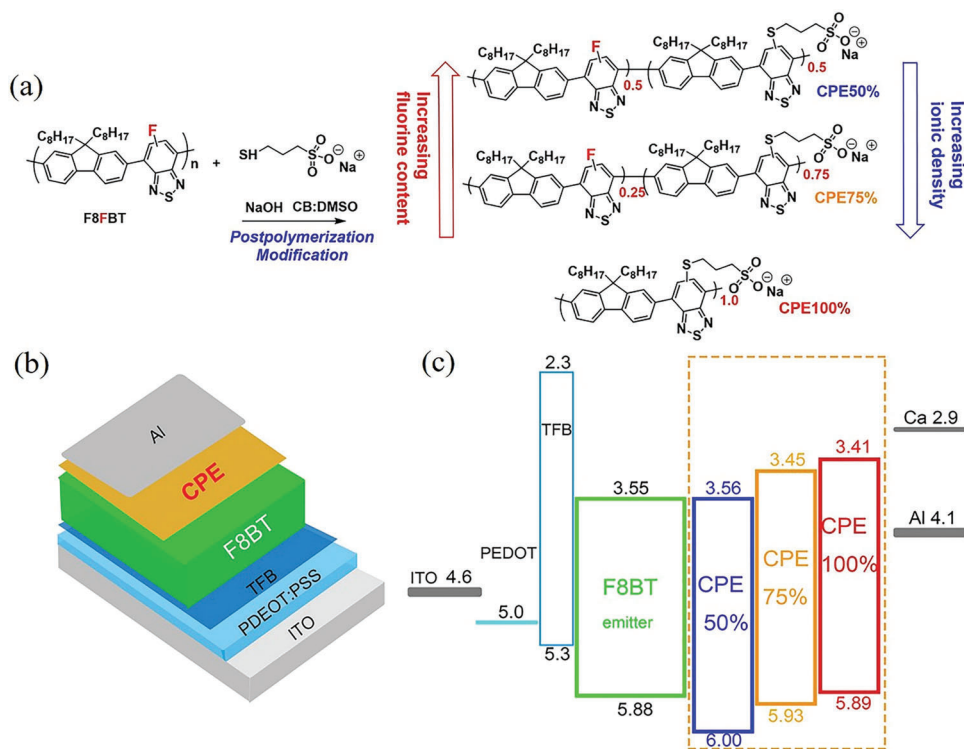


Figure 1. a) Synthesis of CPE-100%, CPE-75%, and CPE-50% from the same batch of polymer F8FBT. b,c) PLED conventional device architecture and energy diagram.

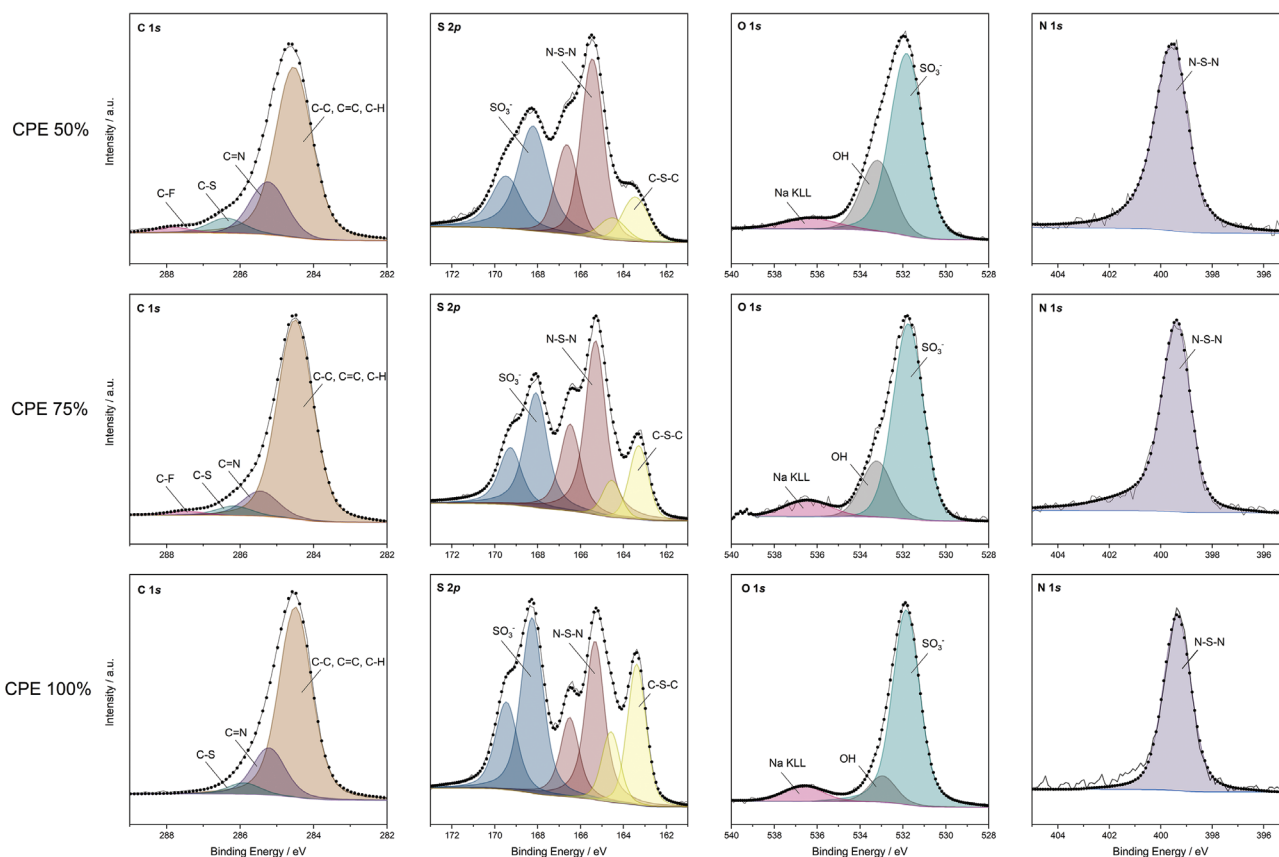


Figure 2. High-resolution XPS spectra of a C 1s, S 2p, O 1s, and N 1s regions for CPE-50% (top), CPE-75% (middle), and CPE-100%.

fitting XPS core-level spectra is listed in Table S1 (Supporting Information) and is in excellent agreement with the theoretical values. The solubility of the polymers changes significantly as a result of the ionic densities. For example, F8BT is soluble in chloroform but not soluble in DMSO, while the CPEs can all dissolve in DMSO instead of chloroform (Figure S10, Supporting Information).

The thin-film characteristics of CPEs are presented in Figure S11 (Supporting information), and the relevant data are summarized in Table S2 (Supporting Information). The three CPEs exhibited two main broad absorption bands, with a peak around 335 nm in the high-energy band and a peak at 455 nm in the low-energy band. As the fluorine atom is substituted by the thioether group, the 2,1,3-benzothiadiazole (BT) acceptor becomes less electron deficient.^[21] Noticeably, a new absorption peak is observed between 360 and 370 nm, increasing in intensity as a function of thioether substitution. The intensity of the small shoulder increases when more fluorine atoms on the conjugated backbone were substituted. The additional intense absorption is due to $N_{\text{sulfur}} \rightarrow \pi^*$ transitions.^[19] The onsets of the absorption spectra of CPE-100%, CPE-75%, and CPE-50% in thin films are at 500, 500, and 509 nm, respectively, resulting in optical bandgaps (E_g) of 2.48, 2.48, and 2.44 eV. Owing to the alternating F8BT conjugated backbone used in the CPEs, the UV-vis absorption and photoluminescence (PL) spectra of neat CPEs were similar to that of neat F8BT. Most importantly, both the absorption and PL spectra of CPEs (8 nm) on top of F8BT (70 nm) bilayer films exhibited a negligible change, indicating no color purity problem of these CPE-based PLEDs. The transient PL in Figure S12 (Supporting information) indicates that the CPEs do not significantly quench the PL emission of F8BT.

To explore the impacts of ionic density variation of these CPEs on device performance, a green-emitting polymer F8BT was chosen in CPE-PLEDs. A conventional PLED device architecture with an 8 nm (± 2 nm) CPE electron injection layer was used in this work, as illustrated in Figure 1b. The energy diagram in Figure 1c shows a systematic shallowing of the LUMO and HOMO levels of CPE as the ionic density of CPE increases from 50% to 100%.^[13,22] Such shallowing of energy levels with a high density of ionic groups might indicate the possible formation of the dipoles and/or ion-induced electrostatic potential shift of the CPE films.

To explore the device performance with CPE interlayers, PLEDs with CPE thickness dependence were fabricated, and their device characteristics are shown in Figure S13 (Supporting information). Four CPE-100% solutions of 1, 2, 4, and 6 mg mL⁻¹ were prepared to fabricate 4, 8, 10, and 15 nm CPE layers, respectively. It is clear to see that PLED with 8 nm CPE-100% from 2 mg mL⁻¹ solution shows the highest current density and luminance, and the highest efficiencies of 14.8 cd A⁻¹. Hence, 2 mg mL⁻¹ CPE was chosen for the subsequent device fabrication. Notice that, PLED performance increased with CPE concentration from 1 to 2 mg mL⁻¹ (thickness from 4 to 8 nm), while PLED performance decreased gradually with the increase of CPE thicknesses from 8 to 15 nm, similar to the optimized thickness as the electron injection interlayer reported in other CPEs.^[8] The microscope image of a working pixel shows uniform and featureless EL emission, indicating good surface coverage of CPEs on top of F8BT.

Figure 3a and Figure S14 (Supporting information) show the current density–voltage–luminance (J – V – L) characteristics of the F8BT PLEDs with different EILs, including CPEs, Ca/Al, and Al-only cathode as references. The reference Ca/Al-based PLED had one order of magnitude higher current density above 3 V than CPE-100%. Considering that F8BT is an electron-dominant emitting material with imbalanced hole and electron mobilities,^[23] the PLED with Ca/Al was dominated by electron current with excess electrons without recombination, resulting in the lowest luminous efficiency (8.5 cd A⁻¹) compared to CPE-LEDs (Figure 3b). The CPE-based devices also have the added benefit of shifting the recombination zone further away from the quenching metal interface.^[10,13,14] Compared to the device with Ca/Al cathode, all CPE-based PLEDs had significantly improved device efficiencies with sharp current turn-on voltages (< 2 V), indicating efficient ohmic electron injection from CPE/Al cathode.^[10,13] The current density of the CPE-50% PLED above 3 V was a factor of ten lower than the CPE-100% PLED. The highest efficiency was achieved by CPE-50% of 20.3 cd A⁻¹, whereas the CPE-100% device had 16.1 cd A⁻¹. Even though CPE-75% PLED had the lowest current density and luminance, the luminous efficiency was still greater than that of the Ca/Al PLED and resulted in 13.0 cd A⁻¹ indicating improved exciton formation and radiative recombination. The electroluminescence (EL) spectra were shown in Figure 3c, which shows the predominant emission from the F8BT emitting layer. As mentioned above, there is no additional PL emission and color purity problems due to the CPE layer on top of F8BT thin film. The reduction in EL at 575 nm of CPE PLEDs compared to Ca/Al device is likely due to the micro-cavity effect by a shift in the recombination zone often reported in PLEDs.^[13,14]

Current and luminance response time is a key criterion for PLED display applications. Here, the transient EL spectra of PLEDs were taken at 5 V and 1 Hz square wave pulses (Figure 3d and Figure S15, Supporting information). All CPE-LED devices had an initial spike at turn-on voltage and repeated in the next pulse, which might be related to an imbalance of charge injection, instead of irreversible degradation.^[13,24] The rise time is defined as the time between the onset of the voltage pulse and the asymptote to the rising edge of the EL reaching the EL maximum value.^[13,14] It reflects the build-up time for the minority carrier density in the recombination zone. We found that CPE-100%, CPE-75%, CPE-50%, and Ca/Al PLEDs all had similar fast rise times (5.4, 4.5, 4.3, and 3.7 μ s, respectively).^[11,13,14,25] The response times of these CPEs are substantially faster than previously reported CPE-based PLED devices (which had response times of > 1 s).^[13,25,26] This indicates that ions do not hinder fast electron injection in CPE devices. Overall, CPE-50% gave the best efficiencies and fastest response time in PLEDs, followed by CPE-100% and CPE-75%.

Interestingly, the CPE-50% PLED device characteristics show a voltage- and driving-time dependence as shown in Figure 4. After cycling the PLED 16 times from -2 to 7 V, the luminous efficiency and power efficiency increased gradually (15 to 20.3 cd A⁻¹, 12 to 20.2 lm W⁻¹) with a decrease in current density (126.4 to 78.92 mA cm⁻²). The device performance remained or decreased after 16 scans due to long-time operation. By plotting luminance as a function of current density as shown in Figure S16 (Supporting information), at the same luminance (e.g., 10 000 cd

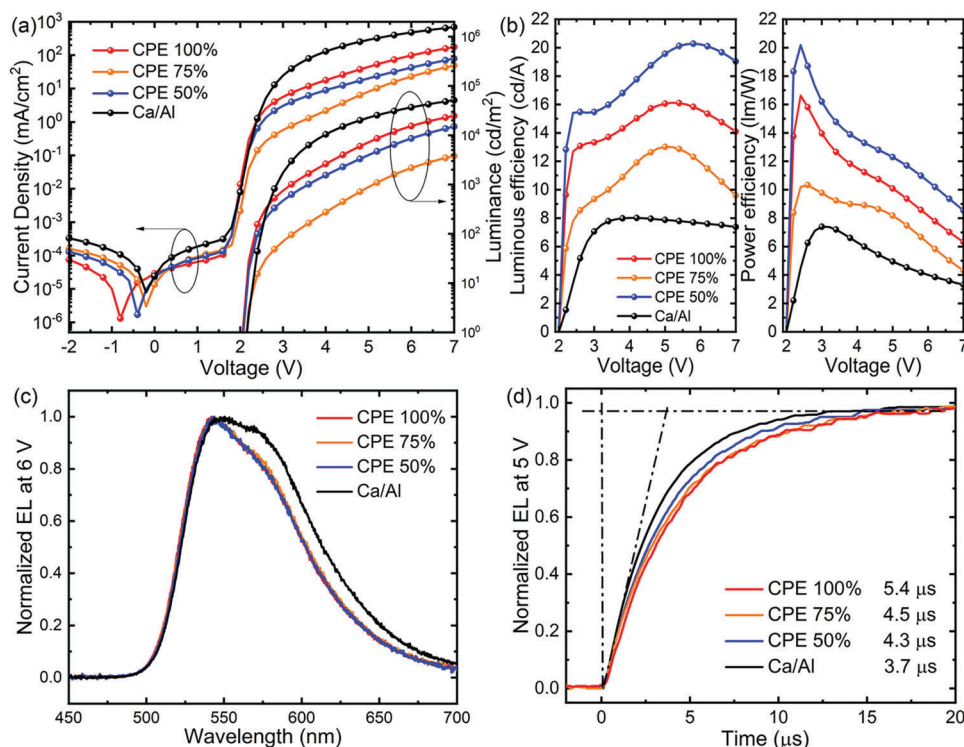


Figure 3. a,b) J - V - L and efficiency of F8BT PLEDs with CPE-100%, CPE-75%, and CPE- 50% electron injection layers and Ca/Al as a reference cathode. c) Normalized electroluminescence (EL) spectra at 6 V. The EL drop at 575 nm of CPEs is due to the microcavity effect or shift of the recombination zone. d) Transient EL and extracted response times at 5 V for the PLEDs.

m^{-2}), the current density decreased gradually from 68.7 mA cm^{-2} (1st scan) to 49 mA cm^{-2} (16th scan). The decrease of current density without changes in luminance indicates more balanced charges and higher recombination, due to efficient blocking of holes in CPE-50% PLEDs. In Figure 4d and Figure S17 (Supporting information), a fresh device was measured under gradually increased maximum operation voltages. Initially, the 0–4 V scan range was applied to the device, which presented a higher luminance turn-on voltage at 2.4 V and a comparatively slow increase of luminous and power efficiencies. At the 0–5 V scan range, the efficiency shape remained stable with relatively poor efficiency in multi scans. Once the scan range was above 5 V, the luminance turn-on voltage shifted from 2.4 to 2.2 V with a sharp efficiency increase and did not show a reversible change. This shifted voltage indicates 200 meV gain of hole injection barrier from the F8BT to CPE-50%, which will enhance hole-blocking performance. These data indicate that the electron current is dominant initially due to nonoptimized CPE orientation. Once voltage stressing above 5 V is applied, the strong electric field can drive ion molecular rearrangement in CPEs and achieve more optimized packing structures, thereby leading to efficient and balanced charge injection.^[10,12]

Figure 5a,b shows the energetic analysis of CPEs by ambient photoemission spectroscopy (APS). The HOMO values of CPEs were extracted by fitting the linear region of APS (Figure 5a and Table S2, Supporting information).^[27] The HOMO of the CPEs gets shallower gradually from CPE-50% to CPE-100% (–6.00, –5.93, and –5.89 eV, respectively), as a result of the replacement of the electron-withdrawing fluorine group with the donating

thioether.^[28] By combining the optical band gap, the LUMO levels of CPEs were estimated to be –3.41 eV (CPE-100%), –3.45 eV (CPE-75%), and –3.56 eV (CPE-50%). The HOMO and LUMO values for the neat F8BT emitter were –5.88 and –3.55 eV, respectively, by the same methodology. This trend is also consistent with DFT calculations of model trimers (Figure S18, Supporting information). To make an ideal electron injection interlayer, both good hole-blocking (deep HOMO) and good electron-injecting (shallow LUMO) properties are important. In the CPE-50% case, the hole-blocking nature with $\approx 0.1 \text{ eV}$ barrier at the F8BT/CPE-50% interface is not sufficient. However, by applying an electric field, the CPE-50% rearranges its ions, increasing the interfacial offset by 200 mV, resulting in a total hole injection offset of about 0.3 eV. This hole injection offset will be enough for efficient blocking of holes, which is similar to efficient electron blocking in PCPDT-K/MAPbBr₃ LED with 0.4 eV electron injection barrier.^[5,15,17,29] The strong hole-blocking properties of CPE-50% were also proved later in SCLC.

To investigate the interfacial dipole formation at the CPE/metal interface, the WF of CPEs on top of Al, Al/F8BT, and Au substrates were measured by Kelvin Probe, as shown in Figure 5c.^[30] The addition of the CPEs on top of Al increased the WF as the ionic density increased, with the most significant change being for CPE-100%/Al which had a 440 meV increased WF compared to bare Al, suggesting the formation of an interfacial dipole with the negative pole toward the CPE polymer layer and the positive pole (Na^+) toward the Al metal (Figure 5d).^[6,31,32] The WF changes for CPE-75%/Al and CPE-50%/Al were 50 and 30 meV, respectively, which might be related

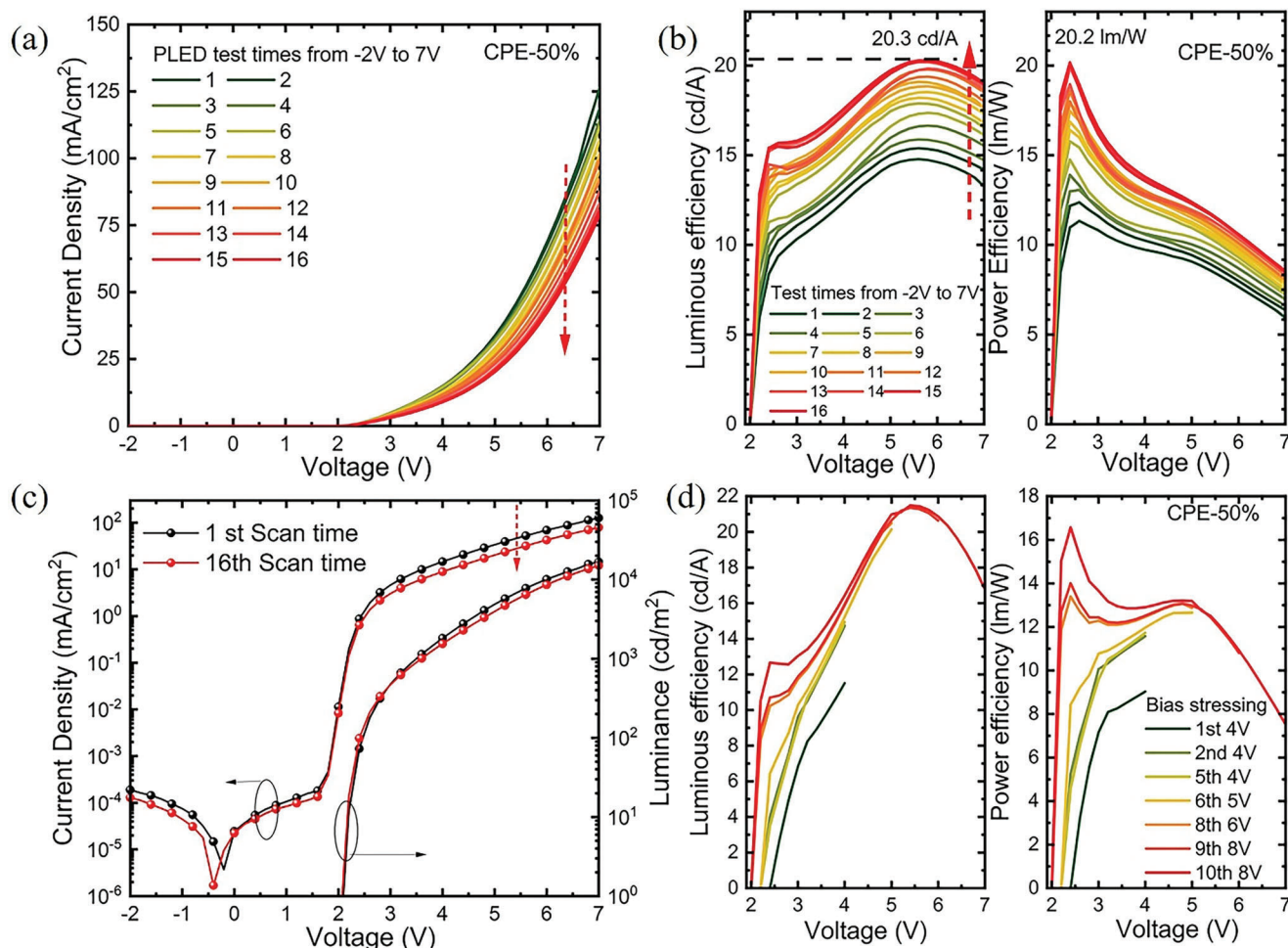


Figure 4. CPE-50% PLED bias-stressing performance in running 16 times from -2 to 7 V. a–c) Current density, efficiency, and J – V – L . d) Maximum operation voltage dependence at 4 , 5 , 6 , and 8 V.

to their lower ionic density, which would be expected to reduce the interfacial dipole strength.^[8,12] Therefore, the interfacial energy barrier between F8BT and Al was finely controlled by modifying the energy levels and ionic densities of CPEs. As CPEs were spin-coated on F8BT before Al deposition in PLEDs, the work functions of Al/F8BT/CPE films were also measured to reveal the dipole arrangement on the F8BT/CPE interface. Similar to Al/CPE, Al/F8BT/CPE-100% had the highest WF (5.17 eV), compared to Al/F8BT/CPE-75% (5.1 eV), Al/F8BT/CPE-50% (5.07 eV), and Al/F8BT (5.06 eV). This suggests the positive pole (Na^+) is towards the F8BT, similar to the CPEs on Al. However, on top of Au substrates, CPE-100% gave the largest work function reduction of the Au substrate (110 meV) because of the strongest dipole strength, compared to CPE-75% (80 meV) and CPE-50% (50 meV).

The inverse trend of WF tuning on Al or Au substrates can be explained by the formation of dipoles in opposite directions in each case.^[14] As the dipole direction of CPE/Al was not favorable and efficient for electron injection, resulting in an enlarged electron injection barrier, there might be a change of ion orientation and dipole rearrangement before and after Al deposition in full PLED devices.^[6,8] As described in Figure 4, the application of

an external voltage to the PLEDs might be the driving force for molecular rearrangement. Interestingly, either on Al or Au substrate, the WF change magnitudes were much smaller than published conjugated polyelectrolytes^[6,8,13,14] or poly ionic liquids.^[10] Nguyen's group published a similar WF change value (40 meV) of PFN- $[\text{SO}_3^-][\text{Na}^+]$, indicating this pendent group may not form strong interfacial dipole regardless of backbone structures.^[32] In addition, these small WF modifications by CPEs, even CPE-100%, cannot make a free-barrier electron injection. However, despite these large electron injection barriers, the J – V – L PLED characteristics of CPEs in Figure 3 exhibit remarkable device performance and ohmic injection with sharp current/luminance turn on, the same as the Ca/Al PLED. Therefore, we consider that the LUMO level matching between CPEs and F8BT plays a minor role in improving device efficiency fabricated with electron-dominant LEPs such as F8BT. The large hole blocking resulting from the deepest HOMO level of CPE-50% is likely the main reason for high efficiency.^[5,17,32,33]

Hole/electron injection and balance are critical to achieving efficient PLEDs, therefore hole-only and electron-only devices with CPE EILs were conducted (see Figure 6). The hole current of CPE-50% was reduced by a factor of 5 relative to Au-only

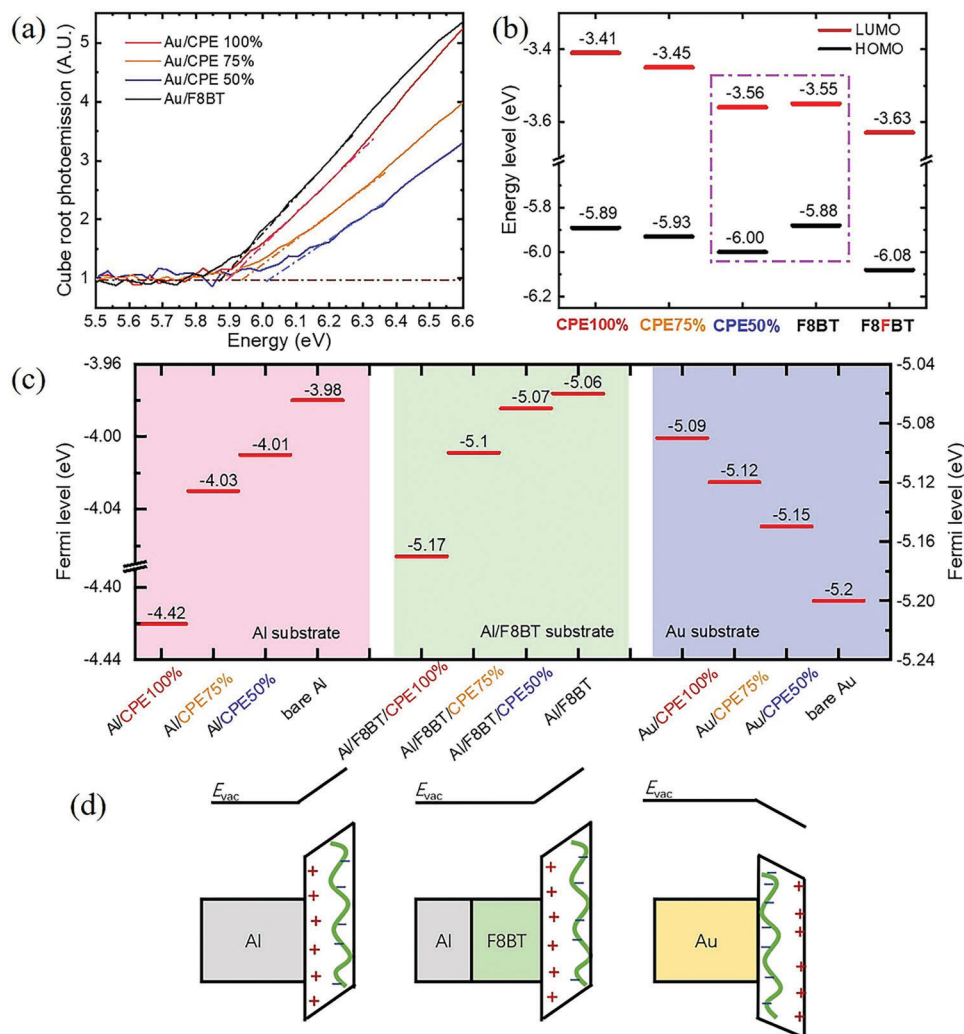


Figure 5. a,b) HOMO and LUMO of F8BT, CPE-100%, CPE-75%, and CPE-50% (all neat film) calculated from ambient photoemission spectroscopy (APS) and energy bandgaps; HOMO/LUMO for F8F8BT are from CV data. c,d) Work functions and dipole directions of CPE on top of Al substrates (pink), Al/F8BT substrates (green), and Au substrates (blue).

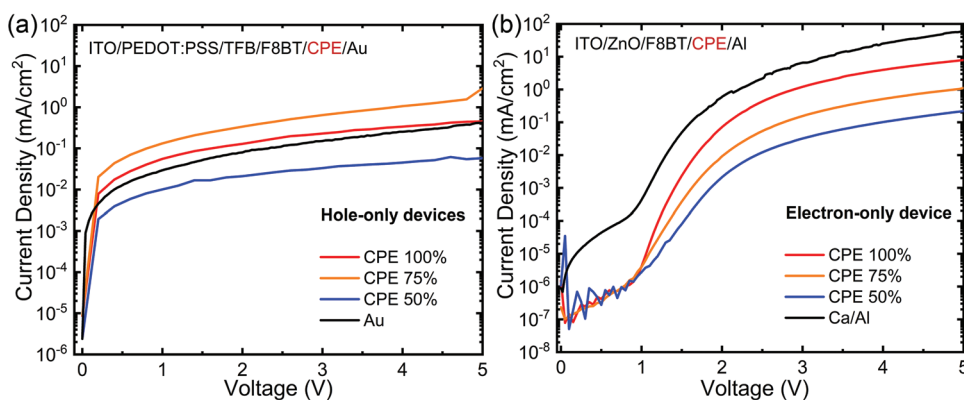


Figure 6. a) Hole-only and b) electron-only devices with CPE-100%, CPE-75%, and CPE-50% as the injection layer. Devices with Au or Ca/Al are used as references. CPE-50% shows the best hole-blocking performance due to the largest F8BT/CPE HOMO band offset.

reference, whereas CPE-100% and CPE-75% had higher hole current than Au. This indicates that CPE-50% is more hole blocking than the others, which can be explained by a combination of the deepest HOMO (-6.00 eV) of CPE-50% and together with the 0.2 eV hole injection barrier increase after the molecular rearrangement. In terms of electron-only devices, PLED with Ca/Al had 25.1 mA cm^{-2} electron current at 4 V and an e/h ratio of 100.84 in Table S3 (Supporting information), indicating large amounts of excess electrons. The electron current densities of all CPE devices were lower than that of Ca/Al and decreased gradually with the decrease of ion fractions. Especially for CPE-50%, the electron current was similar to hole current with an electron/hole (e/h) ratio of 2 . Therefore, PLEDs with CPE-50% had the most balanced charge carriers, resulting in the highest efficiencies.^[34]

3. Conclusion

In summary, we have successfully demonstrated the high-performance F8BT PLEDs with CPEs comprising different FBT and $[\text{SO}_3^-][\text{Na}^+]$ fractions. Importantly, this is the first report describing the systematic design of CPEs with different energy levels and ionic density by postpolymerization method to control charge carrier balance. Postpolymerization modification of substituted FBT can tune both the HOMO level and ionic content simultaneously, allowing optimization of both for better hole/electron balance. Consequently, all CPEs here displayed better performance than Ca/Al reference devices. Owing to the most balanced hole/electron currents and same conjugation backbones, the PLED with CPE-50% EIL shows the highest efficiencies (20.3 cd A^{-1} , 20.2 lm W^{-1}) and the fastest response time ($4.3 \text{ }\mu\text{s}$). Our systematic work emphasizes the importance of charge carrier balance influenced by the conjugated backbone, energetic alignment, and ion fraction of conjugated polyelectrolytes, which gives a strategy for synthesizing efficient conjugated polyelectrolytes. Moreover, we believe that the postpolymerization modification method developed in this work will inspire the molecular design and optimization of conjugated polyelectrolytes for diverse applications.

4. Experimental Section

Materials: F8BT, TFB was synthesized by Cambridge Display Technology (CDT), Inc., UK, and was used as received. The average molecular weight of F8BT was $64\,000 \text{ g mol}^{-1}$. The synthesis details about F8BT and CPEs are given in the Supporting Information.

Solution Preparation: 10 mg neat F8BT was directly dissolved in 1 mL of toluene to yield a concentration of 10 mg mL^{-1} . CPEs were dissolved in DMSO with a concentration of 2 mg mL^{-1} . The CPE solutions were stirred for 24 h at 80°C .

UV-Vis-NIR Absorption and Photoluminescence Spectroscopy and Thin-Film Characterization: Quartz substrates were cleaned using acetone and isopropyl alcohol via sequential sonication for 5 min . F8BT and CPE layers were spin-coated on quartz substrates using the same solutions. The UV-vis absorption was measured using a Shimadzu UV-2550 UV-visible spectrophotometer. PL spectra were recorded in a reflection geometry using a Jobin Yvon Horiba Fluoromax-3 spectrofluorometer (excitation wavelength: 420 nm).

Device Fabrication and Characterization for PLED Applications: ITO-patterned glass substrates (size $12 \text{ mm} \times 8 \text{ mm}$) were cleaned in an ultra-

sonic bath using acetone, isopropyl alcohol, and detergent (Hellmanex, 2% by volume in DI water) for 15 min , followed by washing in DI water twice and baking at 115°C for 10 min . After a 3-min UV-ozone treatment, a 40-nm -thick poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (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 poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl) diphenylamine))] (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 (M_w : $64\,000 \text{ g mol}^{-1}$ and 70 nm thickness) was spin-coated from a toluene solution. Then, an 8-nm -thick CPE layer was spin-coated on top of F8BT and was dried 3 min at 50°C . Finally, aluminum (100 nm) cathodes were deposited via thermal evaporation under vacuum conditions ($1 \times 10^{-7} \text{ Torr}$). For SCLC measurements, F8BT in 15 mg mL^{-1} solution were used to obtain 200-nm -thick layers. The thicknesses of the Au layers deposited by evaporation were 100 nm , respectively.

For the PLED device measurements, the J - V - L characteristics and efficiencies 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 USB 2000 CCD spectrometer equipped with a fiber light collection bundle. All PLED measurements were carried out within a nitrogen-filled test chamber.

APS and SPV Measurements: A KP technology APS-04 instrument was used to evaluate the energetics of neat F8BT, F8BT/CPE, and neat CPEs thin films. For APS measurements, the gold substrate-based sample was illuminated with UV light from a monochromatic deuterium lamp source ($4\text{--}7 \text{ eV}$). SPVs were obtained by measuring the shift in the work function under illumination by a white QTH light source with an intensity of $\approx 20 \text{ mW cm}^{-2}$ and an ON-OFF response time of $\approx 0.1 \text{ s}$. Test samples were organic thin films $\approx 70 \text{ nm}$ thick spin-coated on SiO_2/Au substrates. The metal Au substrate ensured proper grounding of the organic thin films so that correct values of the tip-sample potential difference could be obtained.

Supporting Information

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

Acknowledgements

H.Y. and S.C. contributed equally to this work. The authors acknowledge the UK Engineering and Physical Sciences Research Council (EPSRC), Plastic Electronics Doctoral Training Centre (Grant No. EP/G037515/1), the Royal Society and the Wolfson Foundation, Ministry of Higher Education (MoHE) Malaysia, Chinese Scholarship Council (CSC), and Cambridge Display Technology Ltd. for supplying the F8BT polymers. [Correction added on December 4th, 2023 after first online publication: In Figure 2, the peak labeled as C=O has been corrected to O-H.]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords

conjugated polyelectrolytes, hole blocking, ionic density, PLEDs, postpolymerization modification

Received: April 27, 2023
Revised: May 31, 2023
Published online: July 19, 2023

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