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 μs) 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 biorelated 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 μs.

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 μs). 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. The electron-only devices (EODs) revealed that the insertion of CPE EIL significantly improves electron injection at the interface of F8BT/Al (Figure S7). In particular, the current density of the F8imBT-Br EOD is one order magnitude higher than that of the F8im-Br EOD. Although CPE EILs could offer hole-blocking ability as proved in hole-only devices (Figure S7), high leakage current below the threshold for the PLEDs with CPE EILs seems due to a large amount of injected electrons.[10] 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 cd m^{-2} at 100 mA cm^{-2}, 1.4 times higher than the F8im-Br/Al (11,030 cd m^{-2}) device and 2.2 times the Ca/Al (7,160 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 ~ 26,000 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 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 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] We found that an improvement in device efficiency is not noteworthy for PLEDs with hole-dominant SY-PPV active layer when comparing CPE EILs to Ca EIL (Figure S8). The F8imBT-Br device shows much lower device efficiency than the F8im-Br device in this case; presumably because of the low-lying LUMO level of ~2.7 eV for SY-PPV.[25] This result is consistent with previous literatures.[3, 10, 19]

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.[26] 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.[27, 28] 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.[29]

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 ~ 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 μs) rise in *J* and EL to their peak values followed by a slow decrease (~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 and thus is independent of number of mobile ions in CPE EIL (Figure S9). 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 SY-PPV PLEDs with F8imBT-Br EIL also shows the same quick rise in the transient EL; however the decay is taking place up to ~40 % from the peak (Figure S10). The initial spike is seen for the EL transient in both type of PLEDs (F8BT and SY-PPV) with F8im-Br EIL and it has been observed for other PLEDs with polyelectrolyte EILs, which is generally attributed to ion rearrangement under the applied electric field.[19, 30]

The delay (t_d) and rise time (t_r) values (see Figure S11) 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.[31] 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 zone[31] (Figure S11). 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 (~10^5 μs). 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, 30, 32] 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.[33] 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.[34] Further investigations will clearly be needed to fully understand the mechanism by which our F8imBT-Br CPE EILs lead to efficient and fast response PLEDs and thereby elucidate the design rules for optimal CPE structure.

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 μs) 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) EMLs[35] that have HOMO and LUMO energy levels close to those of F8BT.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental methods including material synthesis and ^{1}H 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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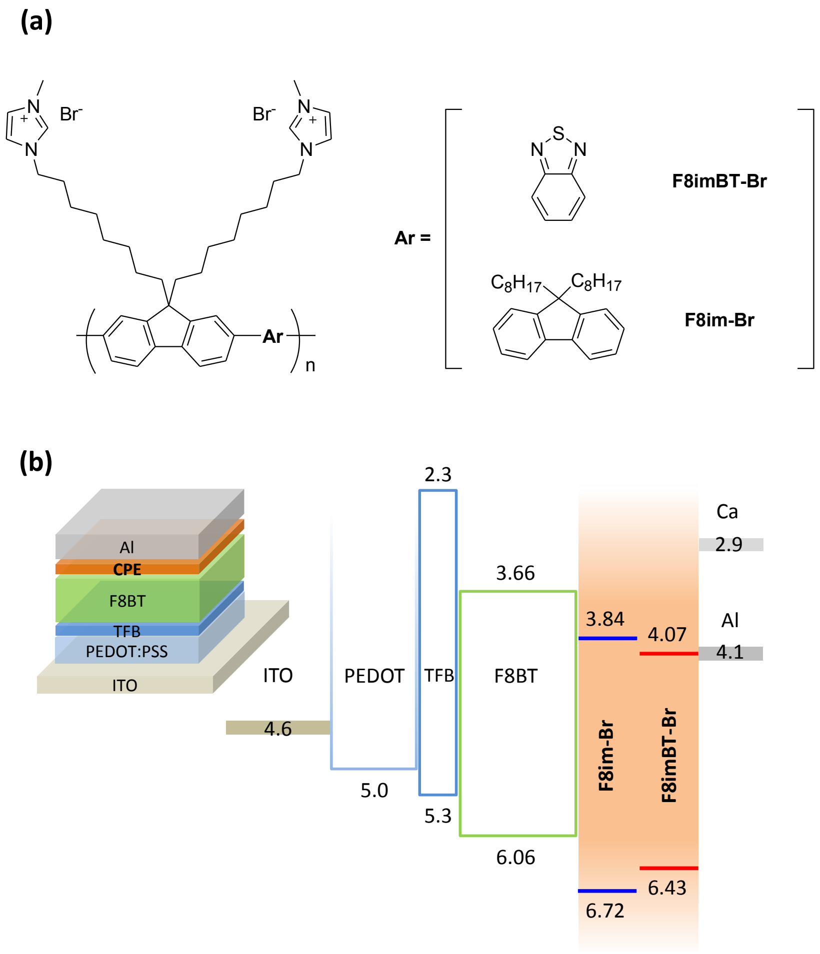

Figure 1. (a) Chemical structures of F8imBT-Br and F8im-Br. (b) Device configuration of F8BT EML PLED and corresponding energy level diagram (in eV).

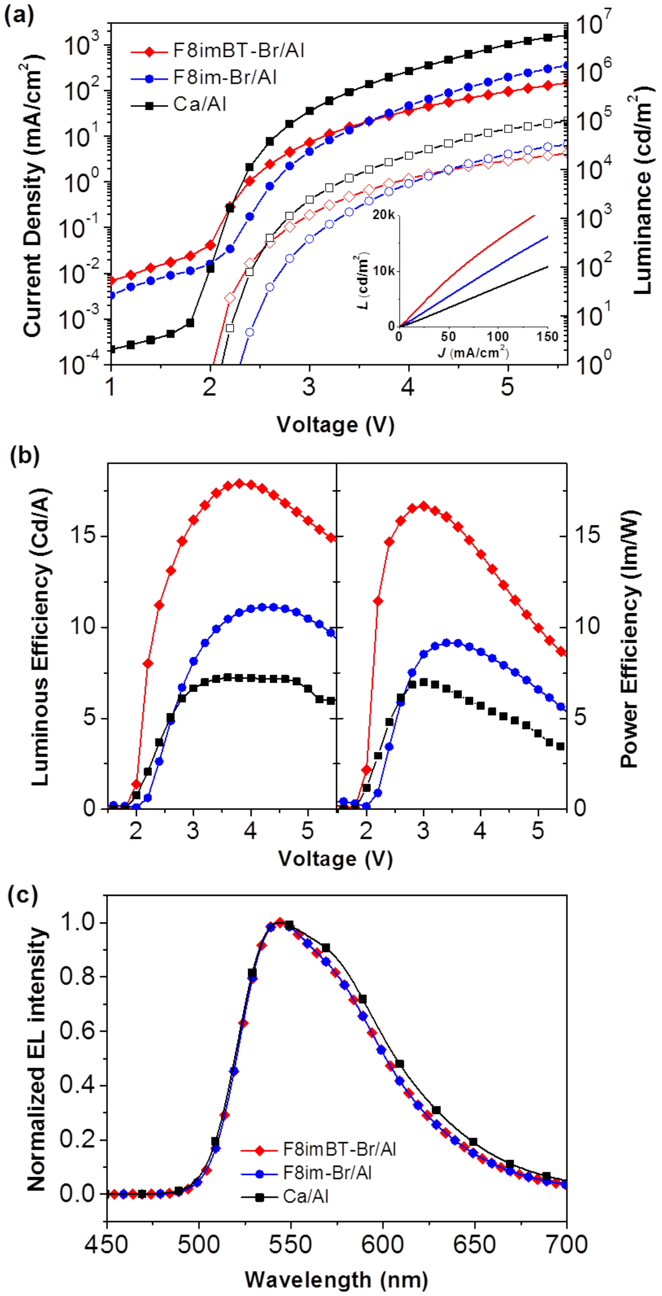

Figure 2. (a) *J*-*V*-*L* characteristics of F8BT PLEDs with F8imBT-Br and F8im-Br EILs; filled symbols are *J*, open symbols are *L*. Data for Ca/Al devices is also shown for comparison. Inset: *L*-*J* curves for all three devices. (b) Luminous (cd A^{-1}) and luminous power (lm W^{-1}) efficiencies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

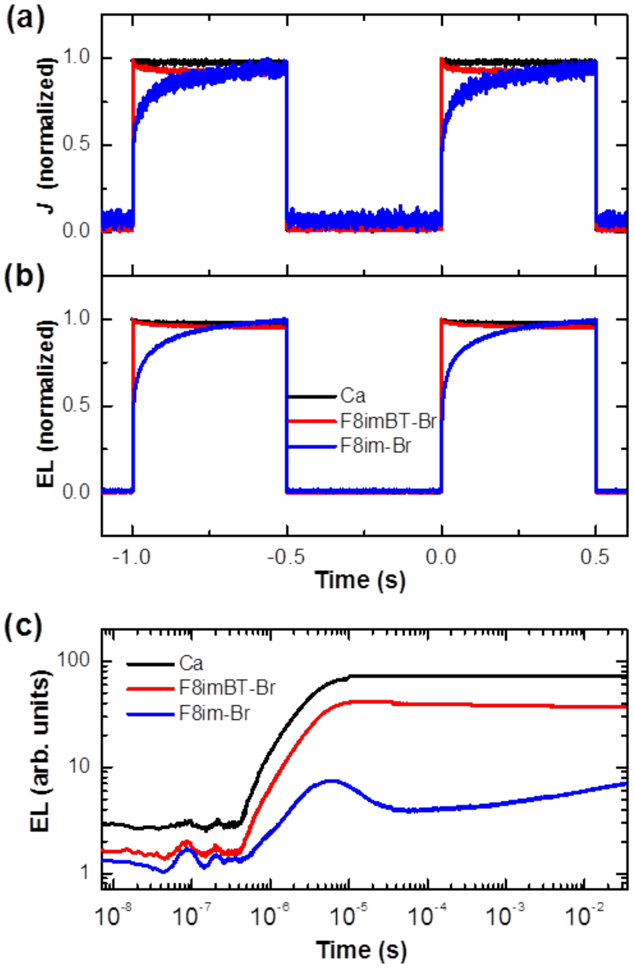

Figure 3. Normalized transient response for the (a) *J* and (b) EL intensity of F8BT PLEDs with F8imBT-Br and F8im-Br EILs. Data for Ca/Al devices is also shown for comparison. (c) Non-normalised EL transient responses for all three PLEDs plotted on a log scale. Data were obtained using 1 Hz repetition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