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## Efficient red electroluminescence from diketopyrrolopyrrole copolymerised with a polyfluorene

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We report the synthesis, characterization, and device incorporation of copolymers based on a common green-emitting polyfluorene but containing a small proportion of a low energy gap donor-acceptor-donor unit for red emission in photo- and electroluminescence. At just 1%–3% random incorporation, the low-gap unit is not present on all chains, yet we demonstrate that efficient charge and energy transfer can yield electroluminescent devices with 1% quantum efficiency and a color that can be tuned by adjusting the density of low-gap units to achieve primary red (National Television System Committee). The high current density tail off in the efficiency is reduced by replacing the hole-injection layer with a photochemically cross-linked electron-blocking layer. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4820433>]

Over a period of more than 20 years, a vast effort has been put into developing materials for organic electronics.<sup>1</sup> Whereas initially significant effort was dedicated to development of blue-emitting materials,<sup>2–5</sup> the focus has recently shifted to low-energy-gap materials for applications as long-wavelength absorbers in solar cells,<sup>6</sup> charge transporters in field-effect transistors,<sup>7,8</sup> as well as red<sup>9,10</sup> and near-infrared<sup>11–16</sup> emitters in organic light-emitting diodes (OLEDs). Many approaches have been proposed to obtain red and infrared emission from organic and solution-processable LEDs, including semiconductor nanoparticles,<sup>17–19</sup> conjugated small molecules,<sup>11–14,20</sup> conjugated polymers,<sup>9,10,21–23</sup> and electrophosphorescence from transition metal<sup>15</sup> and rare earth complexes.<sup>16,24</sup> Of these, rare earth complexes offer some of the highest external quantum efficiencies,<sup>25</sup> with some reports in excess of 20%.<sup>26,27</sup> Nevertheless, polymers are particularly attractive for their solution processability and mechanical flexibility, yet luminescence efficiencies of polymers (and other organic emitters) suffer from high non-radiative decay rates caused by a strong vibrational overlap between ground and excited states.<sup>28,29</sup> Low-gap polymers are also prone to concentration quenching of their luminescence, hence they are often used in low concentrations in blends with a wider gap material,<sup>10,30,31</sup> though this can present a challenge in scaled-up production since phase separation of the components becomes an extra parameter to control. Copolymerization of low-gap molecular units with wider gap hosts may therefore be a more attractive approach.

Here we demonstrate copolymerization of low-gap donor-acceptor-donor (DAD) units with a polyfluorene derivative as an effective method to achieve an efficient low energy gap material for polymer light-emitting diodes (PLEDs) that would be compatible with printing techniques and

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flexible electronics. We further show that by varying the proportion of low-gap DAD units in the chain, we can tune the emission to precisely match “primary red” as defined by the National Television System Committee (NTSC).

One class of low-gap materials that has attracted recent interest in organic electronics is dike-topyrrolopyrrole (DPP) derivatives. These are chemically and thermally stable materials with optical properties tunable by *para* and *meta* position substituents.<sup>32</sup> They have found important industrial applications as dyes, such as *pigment red 254* – known colloquially as “Ferrari red” for its extensive use in automotive paints – but their derivatives have also been investigated as photoluminescent materials<sup>33,34</sup> (including for cellular imaging<sup>35</sup>), dyes in solar cells,<sup>36</sup> sensors,<sup>37</sup> high-mobility ambipolar semiconductors,<sup>36,38</sup> and light-emitting diodes.<sup>39–46</sup> Their use as solid-state emitters has, however, been limited by quenching of the emission by a strong propensity towards aggregation of molecules caused by  $\pi$ - $\pi$  interactions and hydrogen bonding.<sup>47</sup> Consequently, there are very few examples of the development of DPP-only polymers for luminescence,<sup>48</sup> with copolymerization of DPP with wide gap host materials<sup>39–46</sup> being the preferred approach to obtain efficient emissive materials for use in PLEDs. Despite much effort, this relatively successful copolymerization approach still only yields external electroluminescence quantum efficiencies (EQE) of no more than 0.7% (Ref. 45) in the <650 nm spectral region dropping to 0.3% at 670 nm<sup>46</sup>—and often much lower. Furthermore, these efficiencies drop off at the high current densities required in PLEDs.<sup>45</sup> In this work we aim to address these deficiencies.

We copolymerized a DPP-based donor-acceptor-donor unit (Figure 1(a)) with poly(9,9'-dioctylfluorene-alt-benzothiadiazole), F8BT, which has been widely studied for use in PLEDs, and (light-emitting) organic field-effect transistors.<sup>49,50</sup> It was F8BT's relatively balanced electron and hole mobility<sup>50</sup> that led us to select it as the host, to ensure that charge recombination occurs away from the electrodes resulting in a reduction in electrode quenching of the electroluminescence. Indeed, we have previously found F8BT to be a very effective host for infrared-emitting molecules in organic LEDs,<sup>14,21</sup> noting in this work that the highest efficiencies were obtained when diluting the infrared-emitting material to  $\leq 5\%$  of the blend.<sup>21</sup> Along with other groups,<sup>10,41,42,46</sup> we have made similar observations when copolymerizing low-gap DAD emitters with wider gap hosts.<sup>22</sup> Our DPP-F8BT copolymer incorporated into PLEDs demonstrates much improved EQEs of 1% (at 670 nm), and, furthermore, by device design, we eliminate the tail-off in EQE at high driving currents.

The DPP-F8BT polymers were prepared from their three constituent monomer units (F8, BT, and DPP) in brominated form. The monomer [4,7]dibromobenzo[*c*][1,2,5]thiadiazole is commercially available, but in order to be suitable for polymerization it was purified by silica gel chromatography using ethyl acetate as eluent. 9,9'-dioctyl-fluorene-2,7-boronic acid (1,3-propanediol)ester was synthesized according to literature<sup>51,52</sup> and 3,6-bis(5-bromo-thiophen-2-yl)2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)dione was provided by BASF and used without further purification. The three constituent monomers were mixed together and polymerized in a single 24-h palladium catalyzed Suzuki coupling reaction under inert atmosphere. The feed ratios (F8:BT:DPP) for the three polymers were 1:1:0 (F8BT), 0.495:0.495:0.01 (DPP1), and 0.485:0.485:0.03 (DPP3), where DPP1 and DPP3 contain 1% and 3%, respectively, of DPP monomers according to the initial feed ratios. All polymers were purified by washing with sodium diethyldithiocarbamate trihydrate solution (10% by weight) and Soxhlet extraction with methanol, hexane, acetone, and, finally, chloroform. The molecular weight of the polymers were determined by size exclusion chromatography (SEC) using a monodisperse polystyrene standard dissolved in toluene. All the polymers have a  $M_w$  of  $\sim 30$  KDa (Table S1 of the supplementary material). Their thermal stability was checked by thermal gravimetric analysis (TGA), revealing a good stability up to 300 °C for all the polymers.<sup>53</sup>

The low degree of inclusion of DPP units in the polymers DPP1 and DPP3 (1% and 3% based on initial feed ratios of the monomers) means that there will be many polymer chains without any DPP (i.e., they will be just F8BT). In fact if we assume a binomial (i.e., random) distribution of the DPP units across the chains of  $\sim 25$  repeat units we find that 78% of DPP1 chains and 47% of DPP3 chains have no DPP on them.<sup>53</sup> We can therefore consider the active layer as being a blend of DPP-F8BT and F8BT copolymers. As discussed above, this strategy of low DPP inclusion is primarily aimed

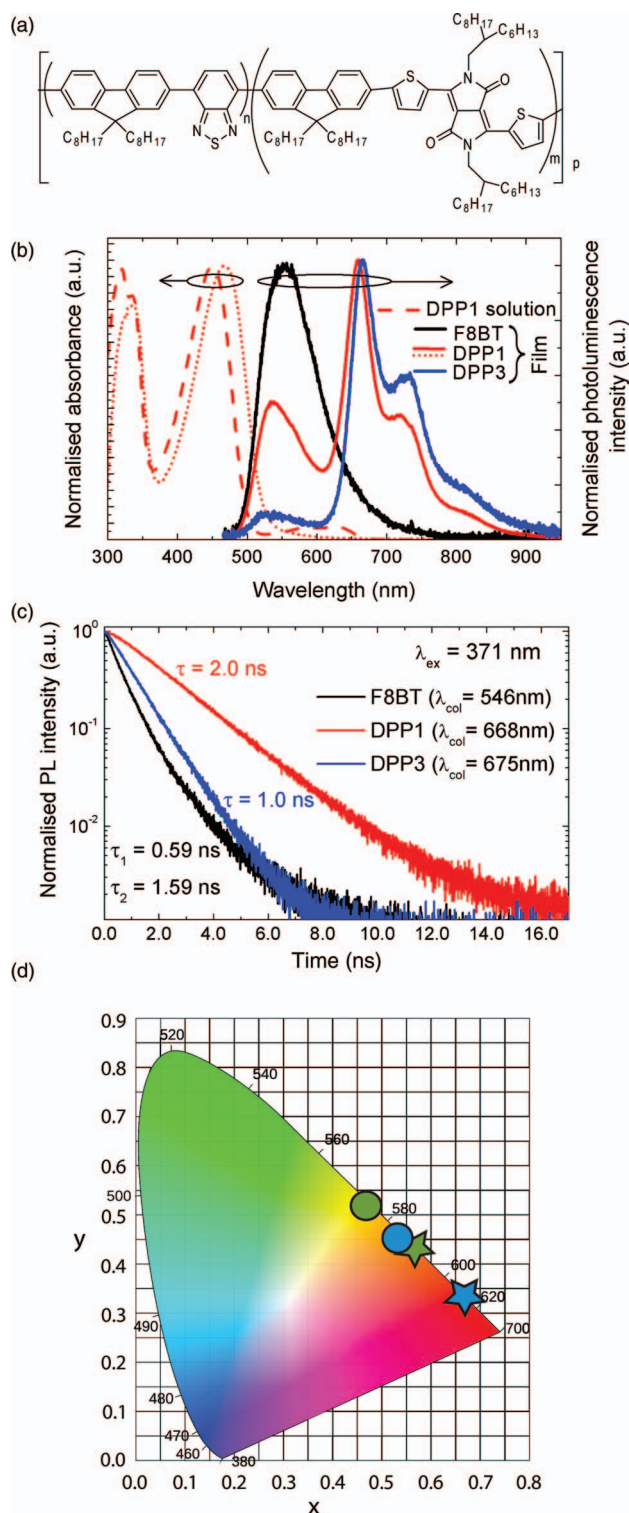


FIG. 1. (a) Chemical structures of the emitting polymers used in this study. Note that F8BT has  $m = 0$ , whilst DPP1 and DPP3 are random copolymers which differ in the ratio  $m:n$ . This ratio is 1:99 for DPP1 and is 3:97 for DPP3. (b) Absorption spectra of DPP1 (red) in solution (dashed) and film (dotted), and photoluminescence spectra (solid lines) of the three synthesized materials in film. Excitation wavelength was 325 nm. (c) Photoluminescence decay of the three materials by excitation at 371 nm. The respective decay times,  $\tau$ , are shown on the plot, along with the collection wavelength,  $\lambda_{col}$ . (d) CIE(xy) color chart plotting the PL (circles) and EL (stars) of DPP1 (green) and DPP3 (blue).

TABLE I. Summary of the photoluminescence and electroluminescence properties of the materials.

	$V_{on}(L)^a$	$EQE_{max,EL}$ (%)	$\lambda_{max,EL}$ (nm)	$CIE(xy)_{EL}$	$R^b$ (mW/cm <sup>2</sup> )	$L^b$ (Cd/m <sup>2</sup> )	$\eta_{PL}$ (%)	$\lambda_{max,PL}$ (nm)	PL lifetime, $\tau$ (ns)	$CIE(xy)_{PL}$
F8BT	$4.5 \pm 0.1$	$0.33 \pm 0.02$	565	...	0.54	340	$29 \pm 3$	565	0.59, 1.59	...
DPP1	$2.9 \pm 0.2$	$0.98 \pm 0.10$	670	(0.57,0.43)	1.41	150	$62 \pm 6$	552, 668	2.0	(0.47,0.52)
DPP3	$3.8 \pm 0.3$	$0.46 \pm 0.30$	670	(0.67,0.33)	1.08	49	$27 \pm 3$	545, 674	1.0	(0.53,0.45)

<sup>a</sup>Defined as the voltage at which light output reaches  $1 \times 10^{-4}$  mW/cm<sup>2</sup>.

<sup>b</sup>Radiance/luminance at a current density of 110 mA/cm<sup>2</sup>.

to reduce the probability of aggregation between DPP units, but our devices can also make use of fast F8BT channels for the transport of electrons and holes away from the electrodes.<sup>49</sup>

The photoluminescence spectra of thin films of the synthesized polymers F8BT, DPP1, and DPP3 are shown in Figure 1(b). The characteristic green emission from F8BT is observed in all cases, though in materials DPP1 and DPP3 this is exceeded in intensity by the red/near-infrared (NIR) emission of the DPP units, which comprises 60% (DPP1) or 94% (DPP3) of the overall emission. The residual F8BT emission is consistent with the model of a low proportion of low-gap units discussed above, where the majority (DPP1) or about half (DPP3) of polymer chains are pure F8BT with no low-gap inclusions. We measured the photoluminescence quantum efficiency (PLQE) of the films using the integrating sphere method,<sup>54</sup> finding values of  $62\% \pm 6\%$  for DPP1 and  $27\% \pm 3\%$  for DPP3. The photoluminescence lifetime (Figure 1(c)) of the DPP units (measured at their peak photoluminescence wavelengths, and not at the peak of the residual F8BT emission) decreases in line with the efficiencies from 2.0 ns (DPP1) to 1.0 ns (DPP3). This decrease in efficiency upon increased DPP loading may be due to aggregation between the low-gap segments, a hypothesis which is supported by a small (6 nm) red-shift in the position of the PL peak.<sup>55</sup> There is also the possibility that in DPP3 there is an increased number of chains incorporating two or more DPP unit in close proximity, resulting in a lower energy-gap of the chain and correspondingly reduced quantum efficiency. A final possibility is that at the higher DPP concentrations exciton migration between DPP segments is possible, allowing excitons that would have been trapped on individual DPP segments at lower DPP concentrations to migrate to quenching sites in films with higher DPP concentrations (noting that molecular conformation differences caused by changing DPP loading could also have a strong effect on intra- and inter-molecular energy transfer<sup>56</sup>). It is worth noting that the host F8BT has a relatively low PLQE ( $29\% \pm 3\%$ ), compared to what we measure for some commercially available ones (American Dye Source,  $73\% \pm 7\%$ ), but that this value is usually highly dependent on deposition conditions (e.g., solvent<sup>57</sup>) and physical properties such as molecular weight. In any case, we are interested in synthesizing an efficient emitter for use in the red/NIR with a suppressed emission from the host. The Commission International d'Éclairage (CIE) 1931 (x,y) color coordinates ( $CIE(xy)$ ) are plotted in Figure 1(d) and are (0.47, 0.52) and (0.53, 0.45) for DPP1 and DPP3, respectively (Table I).

We fabricated LEDs with all three materials. Devices were prepared on glass substrates coated with indium tin oxide (ITO) films, cleaned with an oxygen-plasma<sup>58</sup> before polymer thin film deposition. A PEDOT:PSS hole injection layer (Sigma Aldrich 560596) was spin-coated from 2.8 wt. % dispersion to obtain films  $\sim 75$  nm thick which were then baked at 50 °C for 30 min. 2 wt. % solutions of the above polymers in toluene were prepared and spin-coated on top of the PEDOT:PSS to a thickness of 70 nm. Finally, anodes of 30 nm calcium capped with 150 nm aluminum were evaporated onto the polymer layers to form a number of pixels. Our error bars represent the standard deviation of values obtained from the various pixels.

The current and radiance vs. voltage characteristics of these devices are shown in Figure 2(a) and their electroluminescence spectra in Figure 2(c). The most striking point about the spectra is that the presence of F8BT spectral signals in the copolymer emission is much reduced in the EL (11% for DPP1 and 1% for DPP3) when compared to the PL (40% for DPP1 and 6% for DPP3). In electroluminescence, the migration of charges through the layer gives additional opportunity for trapping of energy on the DPP units,<sup>42</sup> with a resultant quenching of the emission from F8BT.

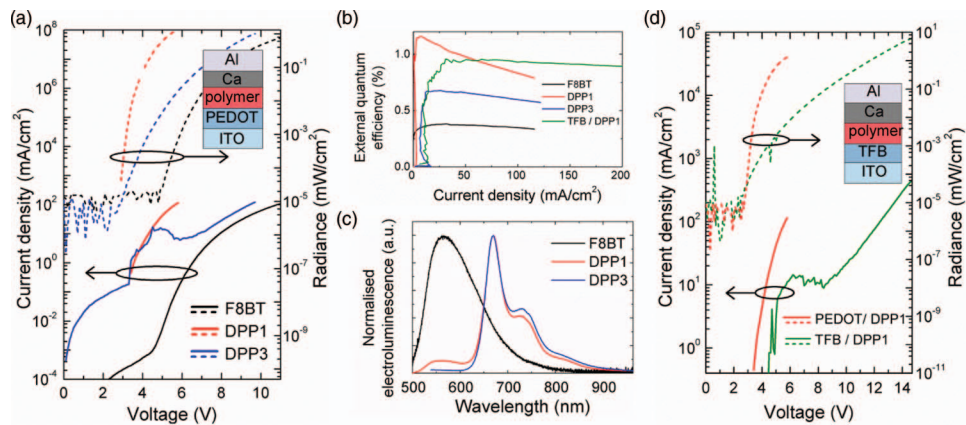


FIG. 2. Light-emitting diode characteristics. (a) Current density (solid lines) and radiance (dashed) plotted as a function of voltage for the device structure using PEDOT:PSS as a hole injection layer, as shown in the schematic (inset). (b) External quantum efficiency of representative devices of each active layer structure, plotted as a function of current density. (c) Electroluminescence spectra of the three synthesized materials. (d) Current density (solid lines) and radiance (dashed) plotted as a function of voltage for the device structure incorporating TFB as a hole injection layer, as shown in the schematic (inset).

Interestingly, this small change in the EL spectrum with increased loading of DPP units allows us to tune the type of red emission from an orange-red for DPP1 (CIE(xy) (0.57, 0.43)) to “primary red” for DPP3 (CIE(xy) (0.67, 0.33)) as defined by the NTSC (Figure 1(d)).

The EL spectra (Figure 2(c)) show essentially no shift in the peak positions compared to the PL spectra. A red-shift is commonly observed in the EL of polymer LEDs compared to their PL since the charges have more opportunity to find lower energy positions on the chain, but in this case the low ratio of DPP units means that they are quite isolated from one another and therefore charges, once trapped on a DPP unit, are unlikely to find lower energy sites within a reasonable hopping distance. The EL quantum efficiencies show a similar trend to the PLQE, with DPP1 having roughly double the quantum efficiency of DPP3 at a value of  $0.98\% \pm 0.10\%$ . This is a substantial advancement compared to the other DPP-based polymers emitting in the  $>650$  nm region, which have not shown efficiencies above 0.3%,<sup>46</sup> and is also higher than DPP-based polymer devices emitting at shorter wavelengths.<sup>45</sup> The corresponding luminances for our devices (at  $110$  mA/cm<sup>2</sup>) are displayed in Table I.

The slow drop-off in efficiency for higher current densities (Figure 2(b)) is indicative of a small charge imbalance in the devices, which is most likely a result of the low electron injection barrier caused by cathode work function pinning<sup>59–61</sup> to the F8BT host LUMO (whereas a sizable, 1 eV or so, injection barrier exists between the anode and the F8BT HOMO). This effect is more noticeable for DPP1 than DPP3, perhaps because the higher DPP concentration in DPP3 causes increased electron trapping in the device or because in DPP3 there is an increased hole-injection directly onto the DPP units which we expect to have a lower barrier to hole injection than F8BT chain segments. In fact, we observe a lower onset of hole current in DPP1/DPP3 devices compared to F8BT devices which does suggest that direct injection onto DPP units may be occurring. As an attempt to boost efficiencies, we replaced the PEDOT:PSS hole-injection layer with a thin polymeric electron blocking layer. Since the LUMO of F8BT (measured as  $-3.3$  eV by cyclic voltammetry<sup>53</sup>) lies below the Fermi level of the calcium cathode ( $-2.8$  eV<sup>62</sup>), we expect the electrode work function to be pinned to the LUMO of F8BT and that there will be no injection barrier for electrons. The Fermi level of the ITO/PEDOT:PSS anode (from  $-4.9$  eV to  $-5.2$  eV<sup>63–65</sup>) on the other hand is far from the F8BT HOMO (measured as  $-6.20$  eV<sup>53</sup>) resulting in a significant hole injection barrier and a charge imbalance in the device. In such cases, electron-blocking interlayers are often included at the anode to boost device efficiencies. In our case, we used poly(9,9'-dioctylfluorene-alt-N-(4-butylphenyl)-diphenylamine) (TFB)<sup>66–69</sup> which has a LUMO of  $-2.1$  eV (HOMO  $-5.35$  eV) as measured by a combination of cyclic voltammetry and optical absorption. The TFB was cross-linked using a UV-activated cross-linker (FPA, see supplementary material<sup>53</sup> and Refs. 65 and 70), which has previously been used to insert TFB interlayers on top of PEDOT:PSS

electrodes,<sup>70</sup> though here we show it can be used directly on top of ITO. The TFB devices showed similar maximum EQE (0.97%) to the PEDOT:PSS devices and similar turn-on voltage, though with higher operating voltages<sup>53</sup> (the operating voltage is known to be a function of TFB thickness due to space-charge resistance<sup>68,70</sup>). Importantly, however, the TFB-interlayer prevents the EQE drop-off at higher current densities observed in PEDOT:PSS devices (Figure 2(b)). This reduced EQE drop-off indicates electron blocking in TFB interlayer devices. At low/medium current densities, electrons in the PEDOT:PSS/DPP1 devices are effectively trapped on the DPP units, preventing flow to the anode without capturing a hole, whilst, at higher current densities where many DPP sites are occupied, EQE tail-off due to electrons passing straight through the device or quenching of excitons formed near the PEDOT:PSS/DPP1 interface increases.<sup>70</sup> The move to a TFB/DPP1 device is therefore beneficial for high current density and high luminance operation.

In conclusion, we have demonstrated an efficient red-emitter, DPP1, based on a small number of DPP-based moieties copolymerized with F8BT, which achieves 1% EL quantum efficiency in PLEDs and 67% solid-state PL quantum efficiency. Our studies have shown that dilution of the DPP on the polymer to just 1% of the monomeric units (a point where not every polymer chain has a DPP unit on it), reduces aggregation effects in a way that is visible in the PL decay times and the PL quantum efficiency. This effect is also visible in the increased efficiencies of the PLEDs at this dilution. Despite balanced hole and electron mobilities in the host F8BT, some drop-off in the EL quantum efficiency can be observed at high current densities for devices with an ITO/PEDOT:PSS anode. This is in line with other studies on DPP-based polymers, but we show that this effect, which is due to an excess of electrons passing through the device and/or pushing of the recombination zone towards the anode, can be eliminated by replacing the PEDOT:PSS with an electron-blocking TFB interlayer. The result is a device which can maintain a 1% EL quantum efficiency at 200 mA/cm<sup>2</sup>. Furthermore, the PLED emission color can be tuned to match NTSC “primary red” by loading the polymer with and increased proportion (3%) of low-gap DPP units.

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