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PAPER

A Diels-Alder crosslinkable host polymer for improved PLED performance: the impact on solution processed doped device and multilayer device performance[†]

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We report on the synthesis of a polyfluorene derivative, **PFO(X)**, with furan pendant groups capable of Diels-Alder crosslinking with a maleimide containing small molecule passive crosslinker (PC) and a maleimide containing red emitting donor-acceptor-donor dopant molecule, **bE-BTD(X)**. It was initially intended that a blend of these three components would afford a system where the dopant concentration could be increased to the point where complete energy transfer from the host polymer to the emissive dopant would be achieved. Because such systems often suffer from quenching and shifts in emission maxima indicative of emitter aggregation, it was hypothesized that crosslinking the emissive dopant with the host polymer would lead to de-aggregation of the dopant emitter. In thin films of **PFO** (X) and **bE-BTD**(X), a 16 nm bathochromic shift is observed in the emission maximum when the dopant concentration is increased from 1% to 8%, suggesting that the dopant is aggregating. In similar films where PC is included and the film is heated to affect crosslinking, a comparable 16 nm shift in the emission maximum is observed indicating that aggregation is still occurring and not affected by the heating step. Similar decreases in luminance are observed independent of whether the heating step is included. Not unexpectedly, however, crosslinking does afford an insoluble network that allows for the subsequent solution deposition of additional layers. When an electron transport layer (ETL) is used in PFO(X)/PC devices, increases of 190% and 490% are observed in luminance and luminous efficiency, respectively, relative to devices without an ETL indicating that this Diels-Alder crosslinkable system is amenable to multilayer deposition by solution methods. When **bE-BTD(X)** is included as the dopant emitter, similar increases in luminance and luminous efficiency are observed with the ETL included compared to devices where this layer is omitted.

Introduction

Conjugated polymer based light emitting devices have been under intense, sustained investigation since the first observation of light emission from a phenylene-vinylene polymer in 1990.¹ Since then, both all-polymer devices and polymer-dopant devices, systems in which a small molecule emitter is doped into a polymer host matrix, have moved forward as attractive alternatives to the classic inorganic- and metal-based devices with polymer materials offering several advantages. For example, polymeric materials offer ease of synthesis, high tunability of electronic properties, and a level of processability that is amenable to the construction of large area devices. When considering that polymer based light emitting diodes (PLEDs) are capable of displaying high brightness with relatively high luminous efficiency they emerge as promising alternatives to the classic inorganic devices.^{2,3}

Although PLEDs are a very attractive alternative lighting source due to their ease of processability, they generally have efficiencies which lag behind those of vapour deposited organic light emitting diodes (OLEDs). This is attributed to two main factors. First, the use of small molecules in vapour deposited devices allows for higher purity materials to be obtained through purification techniques such as sublimation,⁴ and second, the vapour deposition process allows the facile fabrication of multilayer device architectures.^{5,6} These multilayer devices consist of electron transporting/hole blocking and hole transporting/electron blocking layers sandwiching the emissive layer, resulting in devices with external quantum efficiencies of ~20%.^{2,5,7,8} The use of appropriate materials leads to enhanced charge injection and confinement of charges to the emissive layer, thus leading to lower operating powers and reduced efficiency

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losses due to leakage current and non-radiative charge recombination at the electrodes.

The realization of multilayer solution processed PLEDs is significantly more difficult when compared to vapour deposited OLEDs, however, because sequential layer deposition in PLEDs requires either the use of orthogonal solvents^{9,10} to process the different layers or that layers be rendered insoluble after deposition. Due to the similar solubility of electronically active organic materials the use of orthogonal solvents has seen more limited use, the one ubiquitous exception being PEDOT:PSS, which is spin cast from water and is insoluble in common organic solvents thus allowing the solution processing of the active layer. To date, the latter approach has been achieved through either a loss of solubilizing groups¹¹ or through post deposition crosslinking.12,13 The loss of solubilizing groups was famously used in the first demonstration of electroluminescence from poly(paraphenylene vinylene).¹ The use of crosslinking is more versatile, and consequently it is emerging as a promising means of fabricating multilayer solution processed devices as detailed in a review by Marder and coworkers.¹³ Crosslinking can occur thermally or be photo- or chemically initiated and proceed with or without the formation of by-products. Styryl groups, for example, have found use as cross-linkable groups in polymers used in the emissive layer^{14,15} or hole transporting¹⁶ layer. Similarly, trifluorovinylether functionalized polymers have been used where a 2 + 2 cycloaddition upon heating gives a hexafluorocyclobutane group, resulting in a loss in polymer solubility.^{17,18} Some crosslinkable functional groups such as oxetanes¹⁹⁻²² and siloxanes²³ are known to leave side products including photoacid initiator residue (for oxetanes) and water (for siloxanes) which have detrimental effects on device performance. The formation of insoluble polymer networks from soluble and crosslinkable precursors, regardless of crosslinking method, usually affords devices that have enhanced efficiency over single layer devices.^{13,24}

Our group is interested in using conjugated polymer hosts with red to near-IR (NIR) emitting dopant molecules.^{25–28} Using either Förster energy transfer or charge trapping with the appropriate polymer host allows for emission from the dopant molecule.²⁹ In order to obtain complete quenching of host emission a sufficient amount of dopant must be added.^{25,26} At the required dopant levels, unfortunately, small shifts in the emission band and a decrease in device performance (as measured by luminance and luminous efficiency) are both observed. We believe that this phenomenon is the result of aggregation of the dopant molecules, which in some instance has been observed by atomic force microscopy (AFM).²⁵ Therefore, it is necessary to inhibit the aggregation of dopant molecules to achieve higher efficiency devices.

As an analogy to host polymer-dopant emitter systems, nonlinear optical (NLO) systems typically suffer losses in responsivity from aggregation of strongly dipolar chromophores. This problem has been addressed by Jen and coworkers^{30–32} using a combination of heating, poling, and crosslinking through a Diels–Alder reaction to afford devices with enhanced and prolonged nonlinear optical responses. With this in mind, we chose to apply a similar strategy to PLED architectures and devices. The crosslinking approach we have taken was intended to serve two primary purposes, including the reduction of

aggregation and the ability to create insoluble films allowing for solution processed multilayer devices. Additionally, the synthetic approach to crosslinking employed does not require the use of any additional initiators, high temperatures, or exposure to potentially harmful UV irradiation as some previous approaches have required.¹³

Results and discussion

Design strategy

Using the NLO work of Jen for inspiration,^{30,32-34} we envisioned a system composed of a conjugated host polymer with pendant furan groups and a dopant NIR emitter molecule containing the complementary dienophile maleimide; a bis-maleimide passive (non-emitting) crosslinker would also be employed to ensure complete crosslinking as the dopant molecule would only be included at a few weight percent. To the best of our knowledge this Diels-Alder crosslinking approach has not yet been applied to PLEDs and has the advantage that, as a part of the crosslinking process, there are no by-products or reactive intermediates that would lead to degradation of the polymer or emitter. Fig. 1 shows the crosslinking chemistry using maleimide and furan as well our envisioned system with a generic crosslinkable polymer and small molecule crosslinking agent. As with the NLO systems, we hoped that the thermally induced crosslinking step would simultaneously break up dopant molecule aggregates while also "freezing" the dopant molecules in this non-aggregated state (not shown in Fig. 1).

For the initial experiments, as detailed in this manuscript, we chose to use a polyfluorene (**PF**) derivative as our host material. The **PF** class of polymers presents several advantages including a wide bandgap, ease of synthesis, and the ability to include the required crosslinkable pendant groups. The wide band gap is desirable as it should facilitate good energy transfer to the emissive dopant oligomer. We elected to synthesize our **PF** host



Fig. 1 Depiction of the Diels–Alder reaction between furan and maleimide and the crosslinking that would occur in a film composed of a crosslinkable polymer and a separate crosslinking agent.



Chart 1 Molecular structures of the host polymer **PFO(X)**, maleimide containing passive crosslinker **PC**, the red emitting oligomeric dopant **bE-BTD(X)**, and electron transport material **TAZ**.

polymer with furfuryloxy pendant groups to give **PFO(X)** (Chart 1) given the precedence for a Suzuki polycondensation in the presence of furanyl pendant groups.³⁵ Additionally, the Suzuki methodology is one of the most often utilized methods to achieve **PFs**.^{36,37} To ensure effective crosslinking, **PFO(X)** is designed as an alternating copolymer with the 9,9-difurfuryloxyhexyl pendant groups appearing on every other fluorene unit.

Because maleimide is easily reacted in $S_n 2$ fashion with alkyl halide containing compounds, we chose to use it as the corresponding dieneophile in both the passive crosslinker and NIR dopant emitter. The small molecule 1,6-dimaleimidohexane would serve as the passive crosslinker (**PC**, Chart 1). An emissive donor–acceptor-donor dopant oligomer, *bis*-(6-maleimidohexyl) ethylenedioxythiophene-benzothiadiazole (**bE-BTD(X)**, Chart 1), is terminated with maleimidohexane groups that allow this emitter to crosslink as well. For comparison purposes in our study, we also present results obtained from a commercially available poly(9,9-dioctylfluorene) purchased from American Dye Source, **PFO**, which is unable to undergo crosslinking reactions.

Synthesis

As shown in Scheme 1, **PFO(X)** is obtained by the coupling of 2,7-bispinocalatoboron-9,9-dioctylfluorene (1) and 2,7-dibromo-9,9-di(6-furfuryloxyhexyl)fluorene (2) under Suzuki coupling conditions. After the polymerization is allowed to proceed for 48



Scheme 1 Synthesis of PFO(X) and furan containing monomer 2.

hours, end capping is affected by first adding a small amount of the commercially available pinacol ester of phenylboronic acid followed by the addition of bromobenzene. The required monomer 2 was obtained by the reaction of 2,7-dibromofluorene (3) with 1,6-dibromohexane in aqueous sodium hydroxide with tetrabutylammonium bromide functioning as a phase transfer catalyst to give 4, which is reacted with deprotonated furfuryl alcohol giving 2 in 48% yield. PFO(X) was purified by Soxhlet extraction with methanol, hexane, and finally chloroform to obtain the high molecular weight fraction used in devices. Residual palladium was removed with the palladium scavenger diethylammonium diethyldithiocarbamate. The ¹H NMR spectrum and elemental analysis of PFO(X) are both consistent with a polyfluorene containing two furan groups on every other repeat unit. Additionally, gel permeation chromatography (GPC) data shows that PFO(X) has a monomodal molecular weight distribution with an M_n of 38,047 g mol⁻¹ and a polydispersity index (PDI) of 1.87.

While **PFO(X)** initially showed excellent solubility, after a matter of weeks the solubility decreased as evidenced by particulates that were insoluble in chlorobenzene solution, even after heating and prolonged stirring. It is hypothesized that some acidic impurities, known to be present in chloroform,³⁸ contaminated the polymer sample after removal of solvent from the final Soxhlet extraction. As furan is acid sensitive, these acidic impurities may have lead to slow crosslinking between the pendant groups. Though the level of crosslinking is suspected to be low, it was sufficiently high to decrease the polymer solubility. To test this hypothesis, a second quantity of PFO(X) was synthesized and purified as before, the exception being that the chloroform used for the final Soxhlet extraction was distilled from potassium carbonate immediately before use thereby removing any acidic impurities. This second batch has, over a period of several months, maintained its excellent solubility.

The passive crosslinker **PC** was synthesized by slight modification of a previously reported procedure.³⁹ Briefly, furan and maleimide are reacted to give their Diels–Alder adduct (**FM-a** in Scheme 2). This adduct protects maleimide from any base



Scheme 2 Synthesis of crosslinkable, maleimide terminated donoracceptor-donor oligomer **bE-BTD(X)**.

promoted decomposition given that **FM-a** is reacted with 1,6diboromohexane in the presence of potassium carbonate in the subsequent step. The resulting product is then heated to affect a retro Diels–Alder reaction yielding **PC**.

The synthesis of **bE-BTD(X)** is outlined in Scheme 2. Commercially available 3,4-ethylenedioxythiophene (5) is treated with *n*-butyllithium followed by quenching of the anion with **Br-C6-OTHP** to give 6. Compound 6 is then deprotonated with n-butyllithium and reacted with trimethyltin chloride to give stanylated compound 7. A Stille coupling between 4,7-dibromobenzo[c]-1,2,5-thiadiazole (8) and 7 gives tetrahydropyranyl (THP) protected 9. THP protecting group removal is achieved in methanol with catalytic hydrochloric acid to afford dialcohol 10, which is tosylated to give 11. The tosyl group is displaced with FM-a under basic conditions and the crude material heated in toluene to drive the retro-Diels-Alder reaction giving bE-BTD (X) in 47% yield after column chromatography. It should be noted that attempts to isolate **bE-BTD(X)** without a heating step lead to complicated product mixtures owing to the presence of endo and exo isomers of the FM-a component, which have different retention factors.

Thermal characterization

Thermogravimetric analysis (TGA) and differential scanning calorimetery (DSC) were used to examine pure **PFO(X)**, pure **bE-BTD(X)**, and a mixture of **PFO(X)** and **PC**. We observe by TGA that a mixture of **PFO(X)** and **PC** (1 : 1 maleimide:furan) is stable up to 190 °C while **bE-BTD(X)** is stable up to 300 °C, thereby indicating that thermal decomposition would not be a problem during device operation. Additionally, these experiments show that crosslinking takes place in the solid state and the data are provided in the Supporting Information.[†]

The DSC experiments show that pure **PC** has a melting transition at 141 °C, while pure **bE-BTD(X)** shows a melting transition at 128 °C. This **PC** melting transition is observed in the first heating cycle when a mixture of **PFO(X)** and **PC** (1 : 1 furan/ maleimide) is heated from 20 to 180 °C (Fig. 2). This suggests that some crystalline domains of pure **PC** exist in the film and is supported by the surface roughness and crystalline domains observed by AFM; not surprisingly, this crystallinity and roughness is lost on heating of the films as shown in Supporting Information (Figure S1[†]). Two additional transitions are also observed in this first heating cycle, including an exotherm starting at ~110 °C which corresponds to the Diels–Alder crosslinking. This same feature is not observed on the second heating cycle, thereby indicating that crosslinking is complete within the detection limits of the instruments. Observed after the **PC** melt transition is a broad endotherm that is indicative of the Diels– Alder de-crosslinking process (retro Diels–Alder reaction). During the second heat heating cycle this same transition appears but is quite broad. Pure **PFO(X)** shows none of the features observed in the **PFO(X)/PC** blend which supports our assignment of the observed transitions.

Spectral characterization

The spectral characteristics of **PFO(X)** were compared to commercially available **PFO**. Both materials exhibit nearly identical absorption and emission spectra, with $\lambda_{max abs}$ at 388 nm and $\lambda_{max PL}$ at 416 nm for both materials in chloroform as shown in Fig. 3. This suggests that the furan pendant groups do not significantly influence the electronic structure of the polyfluorene backbone through any sort of π - π interactions at the concentrations examined. Thus, we believe that **PFO(X)** will behave similarly to non-crosslinkable **PFO** in our device studies.

To study the effects of the furan pendant groups and the presence of **PC** on the solid-state behaviour of **PFO(X)**, we examined the film photoluminescence spectrum of **PFO(X)** both before and after crosslinking with **PC** and compared it to that of commercially available **PFO** (Fig. 4). Films were spin cast onto **PEDOT:PSS** coated glass substrates with **PFO(X):PC** (1.00 : 0.29 weight ratio) solutions in chlorobenzene, at which there is a 1 : 1 mole ratio of furan to maleimide. Thermal treatment was carried out in an Ar atmosphere glovebox (typically <0.1 ppm O₂ and H₂O) at 130 °C for ten minutes to induce crosslinking. The **PFO** solutions were spin cast from chlorobenzene as well, but were not subjected to the thermal annealing step. A 100 nm thick layer of aluminum was deposited on top of the polymer layer to protect the films from atmospheric water





Fig. 3 Normalized solution absorption and fluorescence spectra of **PFO (X)** and commercially available **PFO** in chloroform.







Fig. 4 Film photoluminescence of commercially available PFO and PFO(X)/PC before and after heating and crosslinking.

and oxygen during photoluminescence measurements, which were performed outside of the glovebox.

Spectral analysis of PFO(X)/PC film emission, presented in Fig. 4, shows small differences when compared to the solution emission spectrum of both PFO and PFO(X), but most importantly demonstrates that the heating and crosslinking processes do not lead to a significant modification in the solid-state emission from the PFO(X)/PC blend. The solid-state photoluminescence spectra of PFO(X) and commercially available PFO do show some differences, with PFO showing broader emission with a more intense 0-1 transition (448 nm) relative to **PFO(X)**. This **PFO** emission spectrum is similar to that of a dihexyl-substituted PF and other PF derivatives previously reported.⁴⁰⁻⁴³ In a study by Bliznyuk and coworkers,⁴⁰ the longer wavelength band was attributed to emission from excimers formed as a result of PF aggregation. This aggregation seems to be minimized in **PFO(X)**, which is likely attributed to the furan pendant groups disrupting intermolecular packing and hence limiting $\pi - \pi$ interactions in the fluorene backbone. This decreased aggregation results in an emission spectrum that is more similar to that of the solution spectra and is consistent with a report by Setayesh⁴³ and co-workers, who examined a PF substituted with dendron side chains. Crystal structure analysis of a model compound and the emission spectrum suggest that aggregation is prevented by the dendrons, which act as shields to prevent $\pi - \pi$ interactions between neighbouring **PF** chains. Keto-defects have also been implicated in the longer wavelength emission bands of PFs, and a report by Bradley and coworkers showed the necessity of close contacts (fluorenone-fluorenone dipole-dipole interaction) for this emission in a series of fluorene oligomers containing fluorenone "defects".44 Work by Veinot45,46 has shown that polyaromatic ethers serve to reduce the dipoledipole interaction in **PF** films. By analogy we believe that the alkyloxyfuran side groups in PFO(X) and maleimide in PC can behave in much the same manner, with the PFO(X) backbone interacting preferably though π -interactions with either furan or maleimide and through dipole-dipole interactions with maleimide thus minimizing the unwanted longer wavelength emission. The overall spectral effect is a more blue emission from PFO(X)/PC films. Additionally, after thermal treatment the peaks/shoulders due to vibrational structure⁴³ become better

defined, presumably due to increased ordering imparted by the thermal treatment. It is also worth mentioning that the **PFO** film is thicker than the **PFO(X)/PC** films, with an absorbance of 0.91 *vs.* 0.36 at 380 nm respectively. The increased thickness of the **PFO** film may result in more self-absorption, thereby increasing the relative intensity of the longer wavelength emission.⁴⁷

Initial device studies

With the solid-state photoluminescence studies indicating that **PFO(X)/PC** films behave similarly to commercially available **PFO**, we turned our attention to electroluminescence studies on films of **PFO(X)** both with and without **PC**, and before and after heating and crosslinking, in a simple device architecture consisting of ITO/PEDOT:PSS/polymer/LiF/Ca/Al. These electroluminescence spectra are presented in Fig. 5. Comparisons are made with an analogous **PFO** device. When biased at 8 V, all films showed strong electroluminescence. Commercially available **PFO** has emission maxima at $\lambda_{max EL} = 435$ nm and 466 nm typical of **PFs**;⁴⁸ the longer wavelength emission between 500 and 600 nm is indicative of aggregation, excimer formation, and/or keto defects as observed in the solid state photoluminescence spectrum in our experiments and as reported previously.^{40,42}

PFO(X) without **PC** exhibits a blue shifted (11 nm, main peak) electroluminescence spectrum relative to commercially available PFO and decreased emission intensity at longer wavelengths. We attribute this observation to the presence of the furan pendant groups, which decrease intermolecular interactions between the PF backbones while also possibly shortening the effective conjugation length due to increased side chain bulkiness.^{41,43} The electroluminescence spectrum of a PFO(X)/PC film shows a further decrease in emission at longer wavelengths when compared to pure PFO(X). This suggests that PC plays a role in breaking up aggregation in PFO(X), thus decreasing excimer formation. Alternatively, the electron deficient maleimide groups in PC could help inhibit the formation of long wavelength emitting keto defects as was observed when PFO is blended with electron accepting oxadiazole containing oligomers and small molecules.⁴⁹ After heating the PFO(X)/PC film a slight blue shift in emission occurs (6 nm, main peak) relative to the unheated



Fig. 5 Electroluminescence spectra of **PFO** (black), **PFO(X)** (red), and **PFO(X)/PC** films with (green) and without (blue) a thermal crosslinking step.

films, which is contrary to the expected red-shift in emission commonly observed after thermal treatment.⁴¹ This blue shift was not observed in the PL spectrum after thermal treatment and its origin is currently unclear.

bE-BTD(X) doped devices

Our original hypothesis was that a thermal treatment and crosslinking step would reduce or eliminate the aggregation of dopant emitter molecules in PFO(X) devices. Towards that goal, we examined the electroluminescence profiles of control devices consisting of **PFO(X)** with **bE-BTD(X)**, no **PC**, and no thermal treatment to induce crosslinking. These control devices were then compared with devices containing PFO(X), bE-BTD (X), and PC in which the films were thermally treated to induce crosslinking and thereby potentially reduce aggregation. The amount of **bE-BTD(X)** was varied from 1 to 8 weight percent and the electroluminescence spectra examined to determine whether or not the heating and crosslinking step would serve to break up aggregation of the dopant emitter. The device architecture consisted of ITO/PEDOT:PSS/active layer/LiF/Ca/Al, where the active layer consists of bE-BTD(X):PFO(X):PC or bE-BTD(X):PFO(X).

The electroluminescence spectra of the control devices are shown in Fig. 6a. Observed is effective but incomplete energy transfer from **PFO(X)** to **bE-BTD(X)** as shown by the strong emission from bE-BTD(X) in the red region of the spectrum. Upon increasing the amount of **bE-BTD(X)** from 1 to 8 weight percent, a 16 nm bathochromic shift in the emission maximum of **bE-BTD(X)** from 636 to 652 nm is observed. Lower concentrations of **bE-BTD(X)** were not applied as these would have resulted in increased PFO(X) emission. The bathochromic spectral shift suggests the formation of aggregates at higher dopant concentrations. With increasing concentrations, a decrease in **PFO(X)** emission is also observed, with minimal PFO(X) emission at 8 weight percent bE-BTD(X). The 1% bE-**BTD(X)** device displays a maximum luminance of 900 cd m^{-2} , whereas the device with 8% bE-BTD(X) displays a maximum luminance of only 220 cd m⁻² as evident in Fig. 6b. The luminous efficiency (η_I) data (Fig. 6c) displays a similar trend as the luminance, with the maximum η_L decreasing from 0.33 cd A⁻¹ for the 1% device to 0.12 cd A^{-1} for the 8% **bE-BTD(X)** device. Given the bathochromic shift observed in the EL spectra upon increasing bE-BTD(X) concentration, it is likely that the decreased device performance is due to aggregate quenching.²⁶ The turn on voltages increase from 4.75 V for the 1% bE-BTD(X) device to 6.0 V for the 8% bE-BTD(X) device. In addition, the current density decreases as the concentration of **bE-BTD(X)** increases as shown in SI Figure S15.[†] This decrease in current likely results from **bE-BTD(X)** or **bE-BTD(X)** aggregates acting as sites for charge trapping in the device.⁵⁰

In an attempt to prevent the spectral modification and decrease in device performance that occurs with increasing dopant concentration, we examined the effects of crosslinking on **bE-BTD(X)** doped **PFO(X)** devices. These devices, after the active layer was spin cast, were heated to $130 \degree C$ for ten minutes in an argon atmosphere glovebox to induce crosslinking. As in the control devices where **PC** was omitted, the concentration of emitter was varied from 1 to 8 weight percent and the



Fig. 6 Electroluminescence spectra (a), luminance-voltage plots (b), and luminous efficiency vs. current density plots (c) for **bE-BTD(X)** doped **PFO(X)** films without **PC**.

electroluminescence spectra, luminance, and luminous efficiency data is presented in Fig. 7.

As in the devices without PC, there is a decrease in PFO(X) emission with increasing concentration of **bE-BTD**(X), but the dopant emitter does not completely quench emission from PFO (X) at the concentrations employed. There is also a bathochromic shift in the emission maximum of **bE-BTD**(X), with $\lambda_{max EL} = 629$ nm at 1% **bE-BTD**(X) and $\lambda_{max EL} = 645$ nm at 8% **bE-BTD**(X), which is a difference of 16 nm just as in the devices without



Fig. 7 Electroluminescence spectra (a), luminance-voltage plots (b), and luminous efficiency vs. current density plots (c) for devices containing **PFO(X)**, **bE-BTD(X)**, and **PC** in the active layer. Crosslinking was affected by heating the devices at 130 °C for ten minutes after spin coating.

PC and no crosslinking (Fig. 7a). The shift in the emission maxima with increasing **bE-BTD(X)** concentration suggests that crosslinking either does not break up aggregates or is not sufficient to keep aggregates from forming as the device cools during the crosslinking step. This supposition is supported by the luminance data as presented in Fig. 7b. This data shows that even after heating and crosslinking the luminance decreases with

increasing **bE-BTD(X)** dopant concentration, with nearly identical luminance maxima as observed for the device with no **PC** as shown in Fig. 6b. The η_L data for the crosslinked devices shown in Fig. 7c indicates the same trend of decreasing η_L with increasing **bE-BTD(X)** concentration; however, the η_L values remain lower at all concentrations when compared to the device without **PC** (0.18 cd A⁻¹ and 0.33 cd A⁻¹ for the 1% **bE-BTD(X)** devices with and without **PC**, respectively). The turn on voltages increase from 5.3 V to 6.0 V as the concentration of **bE-BTD(X)** is increased from 1 to 8%. As with the devices with no **PC**, the current density decreases as the concentration of **bE-BTD(X)** is increased (SI Figure S16†).

Multilayer devices with PFO(X)

800

16

1000

The fabrication of multilayer, all-solution processed organic light emitting diodes is an important topic in the field of organic electronics.¹³ It is known that single layer devices usually offer poorer performance relative to multilayer devices, where dedicated hole transport/electron blocking and electron transport/ hole blocking materials can increase the probability that charge recombination occurs in the desired layer.24 Based on our observation that PFO(X) can crosslink efficiently to give an insoluble network allowing for the deposition of subsequent lavers, we examined its performance as a blue emitter in a multilayered device constructed using the commonly employed electron transport material 3-(4-biphenylyl)-4-phenyl-5-(4-tertbutylphenyl)-1,2,4-triazole (TAZ, Chart 1) in PFO at a ratio of 4:1 by weight.^{51,52} In this device the active layer, consisting of PFO(X) and PC, was spin cast onto the PEDOT:PSS coated substrate, thermally treated to induce cross-linking, and the TAZ:PFO electron transport layer (ETL) spun cast on top. The device was completed by thermal vapour deposition of the LiF/Ca/Al cathode.

To examine whether the addition of an ETL could offer enhanced performance relative to the single layer device, we first assembled devices with PFO(X)/PC as the active layer both with and without the ETL. The luminance and luminous efficiency data for these devices are shown in Fig. 8. While the single layer PFO(X)/PC device shows a lower turn-on voltage, 5.5 V compared to 7.8 V with the ETL, the PFO(X)/PC device with the ETL shows greater luminance at nearly all voltages (Fig. 8a). The higher turn on voltage is expected given that the multilayer device is thicker, thus resulting in a decreased electric field in the device at a specific applied voltage. The maximum luminance reached in the device with the ETL is 2280 cd m⁻² as compared to only 780 cd m^{-2} for the device with no ETL. Concomitant with the increase in luminance is a greater than five-fold increase in luminous efficiency, 1.41 compared to 0.24 cd A⁻¹ upon addition of the TAZ:PFO ETL as shown in Fig. 8b.

The effect of an ETL on the emission of the **bE-BTD(X)** doped devices was probed by assembling devices with **PFO(X)/PC** active layers containing 1 to 8 weight percent of **bE-BTD(X)**. The active layer films were thermally crosslinked as previously described, followed by solution deposition of the **TAZ:PFO** ETL and completed by thermal vapour deposition of a LiF/Ca/Al cathode. The data obtained from these devices are shown in Fig. 9.



Fig. 8 Luminance (a) and luminous efficiency (b) data for PFO(X) devices with and without a TAZ:PFO ETL.

The electroluminescence spectra (Fig. 9a) show incomplete quenching of emission from the host polymer, **PFO(X)** or **PFO**, as in the case of the devices with no ETL; however, when compared to devices without an ETL, the devices with an ETL show greater host emission. This is likely due to emission from **PFO** in the ETL or a shift in the recombination zone to the active layer:ETL interface where the relative concentration of **bE-BTD** (**X**) may be lower. The luminance and η_L data presented in Fig. 9b and 9c clearly show that the devices with ETL layers have increased luminance and η_L with increases from 870 cd m⁻² and 0.18 cd A⁻¹ to 2530 cd m⁻² and 1.8 cd A⁻¹ for the devices without and with an ETL respectively. This corresponds to a ~3 fold increase in the luminance and an order of magnitude increase in η_L upon addition of the ETL.

As was observed for the **PFO(X)/PC** devices upon addition of an ETL, the turn on voltage increases from 5.3 V to 7.8 V for the 1% **bE-BTD(X)** devices upon addition of the ETL. In accordance with the higher η_L , the devices with ETLs display lower leakage currents prior to turn on and decreased operating currents relative to the devices with no ETL (SI Figure S16†). This trend can be explained by the hole blocking nature of the



Fig. 9 Electroluminescence spectra (a), luminance-voltage plots (b), and luminous efficiency *vs.* current density plots (c) for crosslinked **bE-BTD** (X) doped **PFO(X)/PC** devices with a **TAZ:PFO** ETL.

TAZ in the ETL.^{51,52} The observed higher luminance and η_L figures, along with the decreased leakage and operating currents, supports that the ETL helps facilitate charge recombination in the active layer. Importantly, the deposition of the ETL without disrupting the active layer was only made possible through the insolubility of the active layer afforded by crosslinking, something that is not possible with standard **PFO** and other non-crosslinkable **PFs**.

Conclusions

To summarize, a **PF** host polymer with furan pendant groups has been synthesized and interfaced with a maleimide terminated passive crosslinker (PC) and donor-acceptor-donor red emitter **bE-BTD(X)** dopant molecule. Crosslinking and decrosslinking are observed by DSC experiments. We find that heating and concomitant Diels-Alder crosslinking does not lead to reduced aggregation of **bE-BTD(X)** as evidenced by EL spectra. However, we report that crosslinking does allow for the formation of an insoluble network permitting the solution deposition of a subsequent electron transport layer. While the resulting multilayered devices show increased PFO emission, they also show enhanced luminance and luminous efficiency. This approach to the fabrication of multilayered structures has implications for PLED assembly and could lead to all-solutionprocessed multilayer devices with efficiencies equal to that of vapour deposited OLEDs currently available.

Experimental section

Materials and methods

Reagents were obtained from Sigma-Aldrich and purified according to previously published methods before use.³⁸ Furfuryl alcohol was distilled under vacuum from anhydrous potassium carbonate immediately before use; the sodium hydride used was a 60 wt. % dispersion in mineral oil. Compounds 1,53 3,54,55 4,⁵⁶ 6–8,²⁵ and FM-a⁵⁷ were synthesized according to published procedures. PFO(X) was synthesized using usual conditions for the Suzuki polycondensation reaction and the details are given in the supporting information.[†] All NMR spectroscopic experiments were performed on a Varian Gemini 300 Spectrometer operating at 300 MHz for ¹H nuclei and 75 MHz for ¹³C nuclei. Chemical shifts are referenced to CDCl₃ internal standard (7.26 ppm for ¹H and 77.0 ppm for ¹³C). Solution UV-Vis and fluorescence measurements were performed in chloroform on a PerkinElmer Lambda 25 UV-Vis spectrometer and Jobin-Yvon Fluorolog-3 spectrofluorimeter. Elemental analyses were carried out in house. Gel permeation chromatography experiments were conducted on a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 µm PD, 7.8 mm i.d., 300 mm length) using THF as the mobile phase. Differential scanning calorimetry (DSC) was performed using a Thermal Analysis (TA) Q1000 at a heating rate of 10 °C min⁻¹ under helium purge. Calibrations were made using indium and freshly distilled n-octane as the standards for peak temperature transitions and indium for the enthalpy standard. All samples were prepared in hermetically sealed pans and were run using an empty pan as a reference. The samples were scanned for multiple cycles to remove recrystallization differences between samples, and the results were reported from the second scan cycle. Thermogravimetric analysis (TGA) was performed on a TA Q5000 using the dynamic high-resolution analysis. PFO was purchased from American Dye Source with POSS end groups (ADS BE229) and stored in argon atmosphere glovebox (typically <0.1 ppm O₂ and H₂O) until use.

Fabrication and characterization of PLEDS

The multilayer PLEDs were fabricated on 25 by 25 mm prepatterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω/\Box . The substrates were cleaned in ultrasonic baths of sodium dodecyl sulfate in deionized water, deionized water, acetone, and isopropyl alcohol consecutively for 15 min each and then exposed to oxygen plasma for 20 min. Immediately following the substrates were spin coated with a 40 nm thick layer of PEDOT:PSS (Baytron P VP Al4083) and dried at 130 °C on a hotplate in an argon atmosphere glovebox (<0.1 ppm O₂ and H₂O). The active layer was deposited in the glovebox through spin coating a 7 mg mL⁻¹ **PFO** or **PFO(X)** solution in deoxygenated anhydrous chlorobenzene (Sigma Aldrich) or a 9.5–10 mg mL⁻¹ (total weight) PFO(X) + PC + bE-BTD(X)solution in deoxygenated anhydrous chlorobenzene. For all devices individual solutions containing only one material were prepared and stirred overnight, with the PFO and PFO(X) solutions stirred at 50 °C to facilitate dissolution and PC and bE-**BTD(X)** solutions stirred at room temperature. The solutions were then combined and stirred without heating for a maximum of 2 h to avoid crosslinking in solution prior to spin coating. In crosslinked devices the concentrations were adjusted such that the total number of maleimides on bE-BTD(X) and PC combined were equal to the number of furan groups. The devices which were thermally treated were placed on a 130 °C hotplate in the Ar atmosphere glovebox for 10 min. In the multilayer devices the substrates were allowed to cool following heating and then spin cast with a TAZ:PFO (4:1 by weight) layer with a total concentration of 12.5 mg mL⁻¹. All solutions were filtered with 0.45 µm PTFE filters using glass syringes prior to spin coating. A 1 nm layer of LiF, 10 nm layer of Ca, and a 100 nm layer of Al were thermally evaporated at a pressure of 1×10^{-6} mbar through shadow masks to create the cathodes. The pixel areas were 7.07 mm² with each substrate featuring 8 independently addressable pixels. Voltage, current density, luminance, and luminous efficiency characteristics of the PLEDs were measured under ambient conditions using a custom built LabVIEW program with a Keithley 2400 source meter and a UDT Instruments optometer with a calibrated Si photodiode. In combination with the device spectra and cross-calibration with a Minolta CS100 luminance meter, the current measured from the Si photodiode was converted to luminance. EL spectra were taken with an ISA SPEX Triax 180 spectrograph with the devices driven at a constant current using a Keithley 2400 source meter. Luminance and luminous efficiency values reported are the average of 5-6 pixels.

Synthetic details

Compound 9. In an oven-dried flask fitted with a water-cooled reflux condenser was combined compound **7** (1.017 g, 2.08 mmol), compound **8** (0.175 g, 0.59 mmol), and THF. The reaction was degassed by three freeze-pump-thaw cycles, and then Pd (PPh₃)₂Cl₂ (0.020 g, 0.03 mmol) was added followed by a single freeze-pump-thaw cycle. After backfilling with nitrogen and warming to room temperature the reaction was refluxed overnight. Upon cooling to room temperature the reaction was diluted with methylene chloride (100 mL) and washed with

saturated, aqueous NaHCO₃ (2 × 30 mL), brine (30 mL), then dried over MgSO₄. After filtration and removal of solvent under reduced pressure the remaining dark residue was chromatographed on silica eluting with a methylene chloride/ethyl acetate gradient (0 to 4% ethyl acetate). The major compound was isolated and upon removal of solvent a dark, maroon solid was obtained (0.420 g, 90%). ¹H NMR (300 MHz, CDCl₃) δ 8.33 (s, 2H), 4.58 (m, 2H), 4.38 (m, 4H), 4.29 (m, 4H), 3.87 (m, 2H), 3.75 (m, 1H), 3.72 (m, 1H), 3.50 (m, 2H), 3.41 (m, 1H), 3.37 (m, 1H), 2.74 (t, 4H, *J* = 7.7 Hz), 1.82 – 1.43 (m, 28H); ¹³C NMR (75 MHz, CDCl₃) δ 152.2, 140.0, 137.5, 126.1, 123.1, 120.8, 109.6, 98.8, 67.5, 65.0, 64.2, 62.2, 30.8, 30.4, 29.6, 29.0, 26.0, 25.5, 19.7. HRMS (ESI) calculated for C₄₀H₅₃N₂O₈S₃ [M + H]⁺ 785.2959, found *m*/*z* 785.2947.

Compound 10. To a flask containing **9** (0.375 g, 0.48 mmol) was added methanol (4 mL) and dichloromethane (10 mL). With stirring, concentrated hydrochloric acid (2 mL) was added dropwise. The reaction was allowed to stir at room temperature overnight under nitrogen, then poured into methylene chloride (75 mL) and washed with saturated, aqueous sodium bicarbonate (2 × 50 mL) and brine (50 mL). The organic phase was then dried over MgSO₄, filtered, and solvent removed under reduced pressue to afford a dark maroon solid that was spectroscopically pure (0.283 g, 96%). ¹H NMR (300 MHz, CDCl₃) δ 8.33 (s, 2H), 4.37 (m, 4H), 4.30 (m, 4H), 3.65 (m, 4H), 2.74 (t, 4H, *J* = 7.5 Hz), 1.72 (m, 4H), 1.59 (m, 4H), 1.43 (m, 8H), 1.24 (m, 2H). HRMS (ESI) calculated for C₃₀H₃₇N₂O₆S₃ [M + H]⁺ 617.1808, found *m/z* 617.1814.

Compound 11. A round bottom flask was charged with 10 (0.110 g, 0.18 mmol) and anhydrous pyridine (2 mL). The solution was cooled to 0 °C and toluenesulfonyl chloride (0.136 g, 0.71 mmol) was added in a single portion. The reaction was stirred at 0 °C for 2.5 h, then stored at -18 °C overnight at which point TLC showed no starting material. The dark red solution was diluted with ether (150 mL) and washed with aqueous HCl (1M, 4×50 mL) and brine (50 mL). The ether phase was then dried over MgSO₄, filtered, and solvent removed under reduced pressure to give a dark red solid that was further purified on a silica column eluting with methylene chloride. Upon removal of solvent a dark red solid was obtained (0.134 g, 81%). ¹H NMR (300 MHz, CDCl₃) δ 8.34 (s, 2H), 7.78 (d, 4H, J = 8.1 Hz), 7.33 (d, 4H, J = 8.1 Hz), 4.37 (m, 4H), 4.29 (m, 4H), 4.02 (t, 4H, J = 6.5 Hz), 2.69 (t, 4H, J = 7.5 Hz), 2.43 (s, 6H), 1.65 (m, 8H), 1.35 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 152.2, 144.6, 137.6, 133.0, 129.7, 127.7, 126.1, 123.1, 120.3, 109.6, 70.5, 65.0, 64.2, 30.0, 28.7, 28.3, 25.7, 25.0, 21.6. HRMS (ESI) calculated for $C_{44}H_{49}N_2O_{10}S_5 [M + H]^+$ 925.1985, found mlz 925.1944.

bE-BTD(X). A flask was charged with **11** (0.130 g, 0.14 mmol), **FM-a** (0.093 g), and K_2CO_3 (0.078 g) and cooled in an ice bath. Anhydrous DMF (2 mL) was added and the reaction stirred while slowly warming to room temperature overnight, then poured into methylene chloride (100 mL) and washed with water (3 × 50 mL). The organic phase was dried over MgSO₄, filtered, and solvent removed under reduced pressure to give a red solid that was dissolved in toluene and refluxed overnight

to remove the furan protecting group. The solvent was removed under high vacuum and the remaining solid chromatographed on silica eluting with a methylene chloride/ethyl acetate gradient (0 to 8% ethyl acetate). The major eluted spot was collected and afforded a dark red solid upon removal of solvent (0.043 g, 40%). ¹H NMR (300 MHz, CDCl₃) δ 8.32 (s, 2H), 6.66 (s, 4H), 4.36 (m, 4H), 4.29 (m, 4H), 3.51 (t, 4H, J = 7.4 Hz), 2.72 (t, 4H, J = 7.4 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 152.2, 140.1, 137.6, 133.9, 126.1, 123.2, 120.5, 109.7, 65.0, 64.3, 37.9, 30.2, 28.7, 26.5, 25.9. HRMS (ESI) calculated for C₃₈H₃₈N₄O₈S₃ [M]⁺ 774.1846, found *m*/*z* 774.1832. Anal. Calcd.: C 58.90; H, 4.94; N, 7.23; found C, 58.85; H, 4.86; N, 6.92.

1,6-bismaleimidohexane (PC).³⁹ In a flask was combined FMa (1.000 g, 6.06 mmol) and K₂CO₃ (1.190 g, 8.64 mmol). The solids were placed under vacuum for 1 h, and then the flask was backfilled with nitrogen. DMF (15 mL) and 1,6-dibromohexane (0.44 mL, 2.88 mmol) were added and the reaction heated to 40 °C overnight. The now reddish reaction was cooled to room temperature and poured into methylene chloride (200 mL) and washed with water (3 \times 100 mL). The organic phase was collected and dried over MgSO₄, filtered, and solvent removed under reduced pressure to obtain a red coloured solid that was refluxed in toluene overnight. Upon removal of toluene under high vacuum the remaining solid was purified on a short column of silica eluting with methylene chloride to give a white, crystalline solid after removal of solvent (0.422 g, 53%). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta 6.68 \text{ (s, 4H)}, 3.50 \text{ (t, 4H, } J = 7.2 \text{ Hz}\text{)}, 1.58$ (m, 4H), 1.28 (m, 4H).

2,7-dibromo-9,9-bis(6-furfuryloxyhexyl)-9H-fluorene (2). In a 200 mL Schlenk flask was combined DMF (30 mL) and furfuryl alcohol (1.99 mL, 23.1 mmol). The solution was cooled to 0 °C and NaH (60 weight % suspension in mineral oil, 0.923 g, 23.1 mmol) was added in small portions over approximately 30 min. The deprotonation reaction was allowed to stir for an additional 30 min, then compound 4 (2.500 g, 3.85 mmol) was added in one portion. The reaction was stirred for 30 min at 0 °C, then heated to 50 °C overnight. Upon cooling to room temperature the reaction was poured into water (100 mL) and extracted with methylene chloride (4 \times 50 mL). The combined organic phases were washed once with brine (50 mL) and dried over MgSO₄, filtered, and solvent removed under reduced pressure to give a grey-brown oil. The crude product was adsorbed onto silica and chromatographed on silica eluting with a hexanes/ethyl acetate gradient (0 to 15% ethyl acetate). The second eluted compound was collected as a clear, colourless oil upon removal of solvent (1.714 g, 65%). ¹H NMR (300 MHz, CDCl₃) δ 7.51 (dd, 2H, J = 0.5 Hz, 8.0 Hz), 7.44 (dd, 2H, J = 1.7 Hz, 8.0 Hz), 7.42 (dd, 2H, J = 0.5 Hz, 1.7 Hz), 7.37 (dd, 2H, J = 0.8 Hz, 1.8 Hz), 6.32 (dd, 2H, J = 1.8 Hz, 3.2 Hz), 6.27 (dd, 2H, J = 0.5 Hz, 3.2 Hz), 4.37 (s, 4H), 3.34 (t, 4 H, J = 6.6 Hz), 1.89 (m, 4H), 1.40 (m, 4H), 1.08 (m, 8H), 0.58 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 152.2, 151,9, 142.4, 138.8, 130.0, 125.9, 121.3, 121.0, 110.0, 108.8, 70.0, 64.5, 55.5, 40.0, 29.5, 29.3, 25.6, 23.5. HRMS (ESI) calculated for $C_{35}H_{41}Br_2O_4$ [M + H]⁺ 685.1349, found m/z 685.1361. Anal. Calcd.: C 61.41; H, 5.89; N, 0.00; found C, 61.50; H, 5.70; N, 0.00.

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