1. Introduction

Organic light emitting devices (OLEDs) are a rapidly advancing technology due to their applications in full-colour flat-panel displays\textsuperscript{1–4} and energy-saving solid-state lighting,\textsuperscript{5–7} with numerous potential benefits over their inorganic competitors. These benefits include lower power consumption, faster response times, larger viewing angles, smaller sizes and greater ranges of colour and contrast, along with being cheap and quick to produce. OLEDs typically comprise multilayer structures which can give very bright and efficient devices when an emitter layer is sandwiched between additional layers that facilitate hole-transport and electron-transport. However, these multilayer devices have practical limitations as their fabrication is complicated by the need for sequential layer-by-layer deposition procedures. Furthermore, exciplex formation can occur at the organic–organic interfaces, which can be detrimental for efficient and stable emission – especially in the blue spectral region.\textsuperscript{10,11} OLEDs which emit from the deep blue/violet region of the spectrum, especially with Commission Internationale de l’Eclairage (CIE) coordinates that match the National Television System Committee (NTSC) standard blue CIE\textsubscript{xy} (0.14, 0.08) have been the subject of increased investigation to meet the demands of high quality displays.\textsuperscript{12–21} Maximum external quantum efficiencies (EQEs) as high as 3–6\% for emission peaks in the range 400–480 nm have been achieved for a range of small molecule based devices through rational molecular design.\textsuperscript{12,21} However, efficient deep blue polymeric emitters in simple device architectures remain under-developed.\textsuperscript{11,21} Polymeric systems which possess good solubility in organic solvents offer the advantages of rapid industrial-scale polymer LED (PLED) fabrication by solution processing techniques, such as ink-jet printing, spin-coating and roll-to-roll processing.\textsuperscript{22} The key challenge in the molecular design of saturated blue emitting polymers is that backbone conjugation should be restricted to short (oligomer) segments, while the charge carrier transport capabilities of the polymer must be retained.\textsuperscript{23} Poly(9,9-dialkylfluorenone-2,7-diyl) derivatives are widely used as blue/deep blue emitting polymers because of their high charge-carrier mobilities, good thermal and electrochemical stability, high photoluminescence quantum yields (PLQY), and versatile chemical modification.\textsuperscript{24} Specific examples include: poly(3,6-silafluorene-co-2,7-fluorene),\textsuperscript{25} poly(2-fluorene-co-thiophene) host–guest systems\textsuperscript{26} and spiro-polyfluorenes.\textsuperscript{27} Incorporation of tetrafluoro-p-phenylene units into a polyfluorene backbone affords PLEDs with EQEs as high as 5\% with CIE coordinates of (0.16, 0.05).\textsuperscript{28} It has recently been shown that the
attachment of bulky side chains to a polyfluorene backbone increases intrachain torsion angles and isolates minimal conjugated segments. In an alternative approach, 9,9-diphenylfluorene units serve to disrupt conjugation in the polymer backbone leading to PLEDs with EQE values of η\text{PL,max} = 3.9% and \text{i}\text{max} of 274 cd m\text{2} with CIE\text{xy} coordinates (0.17, 0.07). It is also established that meta-linked aromatic units in the backbone can blue shift emission by reducing the effective conjugation length. 

The aim of the present work is to study new readily-available polymers which yield efficient deep blue/violet PLEDs. This has been achieved in two new high triplet energy poly(carbazole-alt-fluorene) co-polymers CF1 and CF2 which function as both the charge carrier transporters and the fluorescent emitters simultaneously. In both polymers the carbazole unit (C) is linked through 3,6-positions, while the linkage to the fluorene unit (F) is varied (2,7 in CF1 – para-conjugated; 3,6 in CF2 – meta-conjugated) in order to modulate the conjugation along the backbone. The photophysics and PLED applications of these co-polymers are reported. In particular, CF1 devices emit deep blue/violet light with remarkably high brightness (\text{i}\text{max} of 565 cd m\text{2}) when the luminosity function is taken into account. The luminosity function shows the perception of brightness to different wavelengths of light, as observed by the human eye and is the function by which OLED emission is normalised. Because the luminosity function peaks at 555 nm, blue and red emission is reduced in comparison to green emission, so more emission is required for these colours to achieve the same brightness. This becomes more of a problem the further the emission is from 555 nm, making the high brightness of CF1 at 409 nm especially notable.

2. Results and discussion

2.1. Polymer synthesis and characterisation

The synthesis of the alternating copolymers CF1 and CF2 (Fig. 1) was carried out under standard Suzuki-Miyaura co-polymerisation conditions followed by end-capping, as described in the ESI. The co-polymers were characterised byGPC-UV-Vis data using polystyrene standards: CF1 \text{M}_\text{w} 31 000 Da, \text{M}_\text{p} 10 800; CF2 \text{M}_\text{w} 21 000 Da, \text{M}_\text{p} 6051 Da. The thermal properties of the polymers were characterised by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere.

The decomposition temperature (\text{T}_\text{d}), which corresponds to a weight loss of 5% at a heating rate of 10 °C min\text{−1}, was 433 °C and 422 °C for CF1 and CF2, respectively, demonstrating that the polymers have very good thermal stability. Glass transition temperatures (\text{T}_\text{g}) of 134 °C and 130 °C for CF1 and CF2 were determined by DSC during the second heating cycle. In addition, no exothermic crystallisation or endothermic melting peaks were observed over the range 40–200 °C, implying that the polymers should exhibit high morphological stability in a device. These data are typical of copolymers of 9,9-dialkylfluorenes and represent increased thermal stability compared to poly(9,9-dialkylfluorene)s, due to the reduced number of alkyl chains in CF1 and CF2. In particular \text{T}_\text{g} is raised significantly compared to poly(9,9-dihexylfluorene) \text{T}_\text{g} 83 °C showing that the N-hexylcarbazole units effectively suppress the dense packing and crystallisation of the polymer chains.

2.2. Optical properties

The spectroscopic data for polymers CF1 and CF2 is summarised in Table 1. Their absorption spectra are shown in the ESI! and their photoluminescence spectra are shown in Fig. 2. The polymers are deep blue/violet emitters (\text{i}_\text{PL,max} in thin films: 421 and 401 nm, respectively). They exhibit very little solvatochromism, in agreement with previous work on fluorene co-polymers, the small changes observed can be explained by the different refractive index of the solvents.

From the photophysical data in Table 2 it can be observed that both CF1 and CF2 emissions peak at ca. 400 nm in solution with negligible solvent polarity effect (Table 2, Fig. 2a and b). Nevertheless, PL from thin films shows a different trend: while CF1 (para-conjugated) shows the typical aggregation induced red-shift (20 nm) in its emission, CF2’s (meta-conjugated) \text{i}_\text{PL,max} remains basically unaltered (Table 2 and Fig. 2c).

No significant difference is observed in the film PLQY for polymers CF1 and CF2, with values of \text{\Phi}_\text{PL} 0.20 and 0.17, respectively. The observed triplet level for CF1 and CF2 (\text{E}_\text{PLD} 2.34 eV) corresponds well to the reported values for poly(9,9-dialkylfluorene) and poly(N-alkylcarbazole) derivatives (ca. 2.3 eV) and related polymers with limited backbone \pi-conjugation.

2.3. PLED device fabrication and properties

Hybrid devices were fabricated with CF1 or CF2 as the spin-coated light-emitting polymer (LEP) layer with the structure: glass\text{ITO (150 nm)}\text{PEDOT:PSS 1.5 (70 nm)}\text{LEP (CF1 or CF2 20 nm)}\text{TPBi (20 nm)}\text{LiF (1 nm)}\text{Al (100 nm)}. For all of the devices, no other
Table 1 Photophysical data for the polymers CF1 and CF2

| Polymer | Solvent/film | $\lambda_{\text{abs}}^{\text{max}}$/nm | $\lambda_{\text{PL}}^{\text{max}}$/nm | PLQY | $E_T$/eV
|---------|--------------|----------------|----------------|------|------|
| CF1     | Ethyl acetate | 348            | 399            |      |      |
|         | Cyclohexane  | 344            | 394            |      |      |
|         | Film         | 350            | 421            | 0.20 | 2.34 |
| CF2     | Ethyl acetate | 300            | 400            |      |      |
|         | Cyclohexane  | 304            | 399            |      |      |
|         | Film         | 287            | 401            | 0.17 | 2.34 |

PLQY is the photoluminescence quantum yield. $E_T$ is the triplet energy determined for solid state samples at 16 K.

Table 2 Electroluminescent device data

|        | $V_{\text{on}}$/V | Brt/cd m$^{-2}$ | EQE/% | Dev eff/cd A$^{-1}$ | Brt$\text{max}$/cd m$^{-2}$ | EQE$\text{max}$/% | Dev eff$\text{max}$/cd A$^{-1}$ | Lum$\text{max}$/lm W$^{-1}$ | CIE$\text{xy}$ | CIE$\text{xy}$ |
|--------|------------------|----------------|-------|---------------------|--------------------------|------------------|-------------------------|-----------------------------|------------|------------|
| CF1    | 3.40             | 232$^{\text{e}}$ | 1.10$^{\text{e}}$ | 0.51$^{\text{e}}$ | 565 (492)$^{\text{d}}$ | 1.4 (2.1)$^{\text{d}}$ | 0.65                     | 0.63                        | 0.16, 0.07 | 0.16, 0.07 |
| CF2    | 4.50             | 16$^{\text{e}}$  | 0.05$^{\text{e}}$ | 0.04$^{\text{e}}$ | 16                      | 0.35             | 0.25                     | 0.99                        | 0.18, 0.12 | 0.20, 0.15 |

$^{\text{a}}$ Device architecture: ITO/PEDOT:PSS/polymer/TPBi/LiF/Al. $^{\text{b}}$ $V_{\text{on}}$ is the turn-on voltage, defined here as the voltage at which the device reaches a brightness of 10 cd m$^{-2}$. $^{\text{c}}$ A comparison current density of 10 mA cm$^{-2}$ was selected. $^{\text{d}}$ Data in brackets are for devices with an additional TAPC layer between PEDOT:PSS and CF1 (see text for details). $^{\text{e}}$ CIE coordinates at the turn-on voltage (10 cd m$^{-2}$). $^{\text{f}}$ CIE coordinates at the maximum brightness. CIE diagrams are shown in the ESI.
conductivity which explains the decrease in the current density passing through the CF2 device, compared to CF1. This reduces both the maximum brightness and EQE of the CF2 device, whilst causing no substantial blue shift in EL emission.

To further investigate CF1, devices were fabricated with an additional hole-injection and electron-blocking layer of 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC). The primary purpose of this layer was to boost device efficiency by preventing electrons from reaching the anode and trapping them in the emissive layer, utilising TAPC’s poor electron mobility. Two TAPC thickness were trialled to give thestructure: glass|ITO (150 nm)|PEDOT:PSS HIL 1.5 (70 nm)|TAPC (60 nm or 90 nm)|LEP (20 nm)|TPBi (20 nm)|LiF (1 nm)|Al (100 nm). Whilst these TAPC thickness are both high relative to the LEP thickness, it was assumed that a portion would be washed away during deposition of the LEP layer leaving a more reasonable thickness behind that could be assessed by ellipsometry. The EQE was raised to $\eta_{\text{ext,max}} 2.1\%$. There was, however, a 25% increase in turn-on voltage and a 13% decrease in the maximum brightness. These were initially believed to be the result of increased device thickness and potential absorption by the TAPC layer, respectively. However, ellipsometry of the multilayer structures returns a combined thickness for the two layers between 19–20 nm. This indicates that the majority of the TAPC layer is removed when the LEP layer is deposited. Despite this, the observed changes in device properties fit with those expected for the addition of an electron blocking layer and so further investigation would be required to determine whether either a very thin film of TAPC remains, or whether the two layers have blended.

4. Conclusions

This work has addressed the synthesis, photophysical characterisation and device properties of two well-defined fluorene-alt-carbazole co-polymers CF1 and CF2 which are deep blue/violet emitters, with $\lambda_{\text{EL,max}}$ 409 nm. The para-conjugated polymer, (CF1), with 2,7-linked fluorene units, is the most efficient emitter, giving PLED devices with external quantum efficiency (EQE) values of $\eta_{\text{ext,max}} 1.4\%$, $L_{\text{max}}$ of 565 cd m$^{-2}$ with CIE$_{x,y}$ (0.16, 0.07). The meta-conjugated polymer, CF2, with 3,6-linked fluorene units, gives analogous devices with $\eta_{\text{ext,max}} 0.35\%$, $L_{\text{max}}$ of 16 cd m$^{-2}$ with CIE$_{x,y}$ (0.18, 0.12). The emission of CF1 devices shows excellent colour stability from 10 cd m$^{-2}$ up to peak brightness, with essentially no shift in the CIE coordinates. The unique combination of a simple co-polymer structure that is based on cheap, readily-available monomer units, low turn-on voltage, excellent colour stability and high brightness in a simple PLED architecture makes CF1 a very promising material for a wide range of applications requiring deep blue/violet emission.
5. Experimental

5.1. Synthesis of polymers CF1 and CF2

The syntheses followed standard routes as reported in the ESI.†

5.2. Optical characterisation

Absorption spectra for solution and solid state samples were obtained using a Shimadzu UV-vis-NIR spectrophotometer whilst emission spectra were acquired using a Jobin-Yvon fluoromax spectrophotofluorimeter. The PLQY data was also obtained using the Jobin-Yvon fluoromax spectrophotofluorimeter, along with a small integrating sphere and a neutral density filter (optical density = 2). The excitation wavelengths were determined from the maximum absorbance of the polymers as obtained from their absorption spectra. The triplet energies of solid state samples at 16 K were calculated using a gated luminescence measurement of the phosphorescence. Solutions were produced in ethyl acetate or cyclohexane, and the OD kept below 1.0. Solid state samples were drop-cast from a 1:1 mixture of 175 mg mL⁻¹ zeonex and 0.5 mg mL⁻¹ of the polymer, both in chlorobenzene, and had a maximum absorbance of 2.0 OD.

5.3. Device fabrication and characterisation

These devices featured an ITO anode (150 nm, 16 Ω⁻¹) commercially pre-coated on a glass substrate (24 mm × 24 mm). The substrates were cleaned with acetone, isopropanol and acetone sequentially in a sonic bath for a period of 9 min each. They were then exposed to low pressure plasma for a period of 3 min and treated with UV-ozone for a further 4 min. A hole-injection layer (HIL) of PEDOT:PSS of thickness 70 nm was deposited by spin coating and then baked on a hotplate at 120 °C for 3 min to remove any remaining moisture. The PEDOT:PSS used was the commercially available HIL 1.5 from Heraeus Precious Metals, Germany. Active layers of polymers CF1 and CF2 were prepared in a solution of chlorobenzene, with the concentration varied to produce layers of 60 nm thickness, and then spun on top of the PEDOT:PSS. The device was then annealed at 120 °C on a hotplate for 10 min to remove residual chlorobenzene. An electron injection layer (EIL) consisting of a 20 nm layer of 1,3,5-tris[N-phenylbenzimidazol-2-yl]benzene (TPBi) was thermally evaporated directly on top of the polymer layer. This was followed by a 1 nm thick lithium fluoride (LiF) cathode, which was thermally evaporated using a shadow mask to produce parallel strips perpendicular to the ITO anodes, forming four individually addressable pixels per substrate each of 5 mm × 4 mm area. The LiF was capped with a 100 nm thick layer of aluminium to protect it from oxidation. An evaporation pressure of the order of 10⁻⁸ mbar and a rate of approximately 0.1 nm s⁻¹ was used for all of the evaporated produced layers. The devices were then encapsulated with DELO UV curable epoxy (Katiobond) and a 12 × 12 mm glass cover slide.

The devices were characterised in a calibrated Labsphere LMS-100 integrating sphere, connected to a USB 4000 CCD spectrometer supplied by a 30 μm UV/Vis fibre optic cable, under steady state conditions. Layer thicknesses were measured using a J. A. Woolam VASE Ellipsometer after having been spin coated onto Si/SiO₂ substrates. The non-uniformity of the organic layer thicknesses across the samples leads to a 5–10% error in device efficiencies: all measurements were averages from at least four devices.

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