## Enhanced electron injection and efficiency in blended-layer organic light emitting diodes with aluminium cathodes: new 2,5-diaryl-1,3,4-oxadiazole– fluorene hybrids incorporating pyridine units<sup>†</sup>

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This work focuses on the first 2,5-diaryl-1,3,4-oxadiazole-fluorene hybrids which incorporate pyridine units within the  $\pi$ -electron system, viz. 2,7-bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2-pyridyl}-9,9-dihexylfluorene (6) and 2,7-bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2-pyridyl}spirobifluorene (7). The thiophene analogue 2,7-bis{5-[5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl]-thien-2-yl}-9,9-dihexylfluorene 11 was also synthesised and its X-ray crystal structure was obtained. There is a progressive red shift in the UV-Vis absorption and photoluminescence spectra on replacing benzene (8) with pyridine (6) and thiophene (11) consistent with increased planarity of the  $\pi$ -system and reduced HOMO-LUMO gap along the series. Calculations at the DFT (density functional theory) level establish that inclusion of the pyridyl rings in 6 and 7 considerably enhances the electron affinity of the system, compared to phenyl analogues. Single-layer organic light-emitting diodes (OLEDs) have been fabricated by spin-coating blends of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) as the emissive material with added electron transport compounds 6 or 7 to enhance electron injection. The external quantum efficiencies of the devices were greatly enhanced compared to pure MEH-PPV reference devices. ITO/PEDOT: PSS/MEH-PPV: 7 (30: 70% by weight)/Al devices exhibited an external quantum efficiency (EQE) of 0.5% and a luminous efficiency of 0.93 cd A<sup>-1</sup> at 9.5 V and a luminance of 100 cd m<sup>-2</sup>. The modest increase in efficiency for the same device when Al was replaced by a Ca/Al cathode (EQE 0.6% and 1.2 cd A<sup>-1</sup> at 10.5 V) suggests that the two methods of enhancing electron injection into the MEH-PPV emitter are mutually exclusive. Utilising blended layers is an attractive alternative to using Ca electrodes, which are highly reactive and are unstable in the atmosphere.

## Introduction

Intense interest in the synthesis and properties of new materials for incorporation into organic light emitting diodes (OLEDs) for display applications<sup>1</sup> has been sustained since the discovery of electroluminescence (EL) in low molecular weight organic molecules<sup>2</sup> and in conjugated polymers.<sup>3</sup> The most widely studied emissive polymers are derivatives of poly(phenylenevinylene) and poly(fluorene). These are predominantly holetransporting (*i.e.* p-dopable) materials which possess low

<sup>b</sup>School of Engineering and Centre for Molecular and Nanoscale Electronics, University of Durham, Durham, UK DH1 3LE. E-mail: m.c.petty@durham.ac.uk electron affinities. In a device structure this creates an imbalance of electron injection (from the low work-function cathode) and hole injection (from the high work-function anode) which leads to charge recombination occurring near the polymer/cathode interface and a lowering of EL efficiency due to quenching of excitons by the metal electrode. A strategy which has proved successful in mitigating this problem is to incorporate electron-deficient (n-type) polymeric or low molecular weight materials into the devices, often as an additional electron-transporting hole-blocking (ETHB) layer, or in some cases as a blend with the emissive polymer.<sup>4</sup>

2,5-Diaryl-1,3,4-oxadiazole (OXD) derivatives are electrondeficient systems which possess good thermal and chemical stabilities and high photoluminescence quantum yields,<sup>5</sup> and this combination of properties has led to their use as ETHB materials in OLEDs.<sup>6</sup> We have recently reported that OXD derivatives enhance electron injection in single-layer devices as blends with poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH–PPV) as the emissive material.<sup>7</sup> The present study is focused on new OXD analogues **6** and **7** in which pyridine rings are incorporated into the conjugated  $\pi$ -system. Pyridine is an electron-deficient heterocycle, so its presence is expected to increase the electron affinity compared

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<sup>†</sup> Electronic supplementary information (ESI) available: B3LYP/6-31G(d) optimised geometries (figures and tables of coordinates); orbital energy level diagrams and frontier orbital localisation for compounds **6a**, **7a**, **6a-iso** and **7a-iso**; X-ray crystallographic data for compound **11** and a diagram and discussion of its crystal structure. See DOI: 10.1039/b510003h

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to OXD.<sup>8</sup> Thiophene analogue **11** was synthesised to probe the effect of heterocycle substitution on the UV–Vis absorption and photoluminescence properties. Density functional theory (DFT) calculations (see below) established that compound **6a**, with the pyridyl nitrogen adjacent to the fluorene, is a stronger electron acceptor than its isomer **6a-iso** which has the pyridyl nitrogen adjacent to the oxadiazole ring. Therefore, we chose the former system as our synthetic target.

Our strategy was to combine the strong electron-transporting ability of the 2-phenyl-5-pyridyl-1,3,4-oxadiazole units with a 9,9-dihexylfluorene core unit to provide blue emission<sup>9</sup> and to utilise energy- or charge-transfer processes within blended layer films to improve further the efficiency of the OLEDs. The attraction of single-layer blended devices of this type is that their manufacture requires only a single spincoating process.<sup>10</sup> Comparisons of **6** and **7** with **8** and **9** show that the pyridyl rings of **6** and **7** have a significant and beneficial effect on the optoelectronic properties of the devices. Comparisons with compound **11** show that the absorption and photoluminescence properties can be tuned by heterocycle substitution in the backbone.

#### **Results and discussion**

#### Synthesis

The 2-phenyl-5-pyridyl-1,3,4-oxadiazole ring system has not been reported previously. The route to compound 3 and its subsequent conversion into the target ETHB materials 6 and 7

is shown in Scheme 1. 6-Bromonicotinic acid 1 was synthesised from 2-bromo-5-methylpyridine following the literature procedure.<sup>11</sup> The reaction of compound **1** with thionyl chloride at reflux gave 2-chloropyridine-4-carbonyl chloride which was reacted directly with 4-dodecyloxybenzoic acid hydrazide 2 in pyridine to give the intermediate dihydrazide which was not purified. In situ dehydrative cyclisation in refluxing phosphorus oxychloride,<sup>12</sup> followed by reaction with HBr in glacial acetic acid (to convert the 2-chloro substituent to 2-bromo) gave the functionalised 2-phenyl-5-pyridyl-1,3,4-oxadiazole reagent 3 in 37% yield from 1. Two-fold reactions of 3 with 9,9-dihexylfluorene-2,7-diboronic acid 413 or the dipinacolboronate reagent 514 under palladium-catalysed Suzuki-Miyaura conditions gave the target compounds 6 and 7. respectively, in 35% and 56% yields. The spirobifluorene core of 7 was chosen because it is known that it can be advantageous in eliminating the formation of fluorenone defects which occur in some fluorene derivatives during device operation; such defects act as charge traps and impair device performance.<sup>15</sup> The dodecyloxy chain was attached to ensure good solubility in organic solvents at all stages of the synthesis.

The thiophene analogue 11 was similarly obtained by two-fold reaction of 4 with compound  $10^{16}$  (Scheme 2).

The X-ray molecular structure of **11** was determined.§ The most notable feature is that the interplanar angles between the outer 6-membered rings of the fluorene moiety and the adjacent thiophene rings vary from 4.6 to  $36.4^{\circ}$ , but on



Scheme 1 Reagents and reaction conditions: (i) 1, SOCl<sub>2</sub>, reflux; then add 2, pyridine, reflux; then POCl<sub>3</sub>, reflux; then DCM, HBr (33% in glacial acetic acid) 37% yield; (ii) 4, Pd[PPh<sub>3</sub>]<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, THF, reflux, 48 h, 35% yield; (iii) 5, Pd[PPh<sub>3</sub>]<sub>4</sub>, tri-*tert*-butylphosphine, K<sub>2</sub>CO<sub>3</sub>, toluene, 80 °C, 48 h, 56% yield.



Scheme 2 Reagents and reaction conditions: (i) 4, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, tri-tert-butylphosphine, Na<sub>2</sub>CO<sub>3</sub>, THF, reflux, 96 h, 42% yield.



average are smaller than the corresponding angles in  $\mathbf{8}$ ,<sup>7b</sup> which has benzene rings instead of thiophene. For a more detailed discussion see the ESI.

#### Theoretical calculations

DFT calculations were performed to elucidate the geometry and the electronic state of the new pyridyl-containing derivatives **6** and **7** in comparison with previously studied ET compounds **8** and **9**.<sup>7b</sup> To decrease the computational time, calculations were performed on molecules **6a** and **7a** (where index "**a**" means that  $C_{12}H_{25}O$  was replaced by  $CH_3O$ , and  $C_6H_{13}$  was replaced by  $C_2H_5$ ; see ESI†). Calculations were also performed on the geometrical isomers of compounds **6a** and **7a**, with different substitution positions at the pyridine rings (compounds **6a-iso** and **7a-iso**).

The optimised geometries of compounds **6a-iso** and **7a-iso** are generally similar to the previously reported benzene analogues **8a** and **9a**, whereas the reduced steric hindrance between the pyridine and fluorene rings in **6a** and **7a** results in substantial planarisation of the system and consequently an increase in the conjugation (see Fig. S4 in ESI<sup>†</sup>). Thus, the

<sup>§</sup> The single-crystal X-ray diffraction experiment was carried out on a Bruker SMART 3-circle diffractometer with an APEX CCD area detector, using graphite monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a 60 W Mo-target microfocus Bede Microsource® X-ray generator with glass polycapillary X-ray optics and a Cryostream-Plus open-flow N<sub>c</sub> cryostat. The structure was solved by direct methods and refined by full-matrix least squares against  $F^2$  of all reflections, using SHELXTL 6.14 software (Bruker-Nonius AXS, Madison, WI, USA, 2003). Crystal data: C<sub>57</sub>H<sub>62</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>, M = 899.23, T = 120 K, triclinic, space group  $P\overline{1}$  (no. 2), a = 16.095(2), b = 16.647(2), c = 19.390(2) Å,  $\alpha = 82.61(1)$ ,  $\beta = 87.70(1)$ ,  $\gamma = 72.94(1)^{\circ}$ , U = 4925(1) Å<sup>3</sup>, Z = 4,  $D_c = 1.213$  g cm<sup>-3</sup>,  $\mu = 0.15$  mm<sup>-1</sup>, 47.733 reflections ( $20 \le 50^{\circ}$ ), 17.322 unique,  $R_{int} = 0.093$ , R = 0.048 [6940 data with  $F^2 \ge 2\alpha(F^2)$ ],  $wR(F^2) = 0.147$  (all data). CCDC reference number 282827. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510003h



Fig. 1 B3LYP/6-311G(2d,p)//B3LYP6-31G(d) frontier orbitals of compounds 6a and 6a-iso.

dihedral angles between the pyridine and fluorene rings in compounds **6a** and **7a** are  $15.5^{\circ}$  and  $16.3^{\circ}$ , respectively, whereas these angles in **6a-iso** and **7a-iso** are  $36.4^{\circ}$  and  $36.5^{\circ}$ , respectively, which are similar to those between the fluorene and adjacent benzene rings in **8a** and **9a**, *viz*.  $35.9^{\circ}$  and  $36.3^{\circ}$ , respectively. All six structures show planarity at the oxadiazole site; the dihedral angles between the oxadiazole moiety and the adjacent benzene and pyridine rings are less then  $1^{\circ}$ .

The localisation of the HOMO and LUMO orbital coefficients for compounds with different substituents at position 9 of the fluorene moiety is quite similar for both series, *i.e.* **6a**/**7a** and **6a-iso**/**7a-iso**. The main population of the HOMO is on the central aromatic fluorene moiety with some extension onto the pyridine and oxadiazole moieties, and quinoidal character of the LUMO orbital (see Fig. S5 and S6 in ESI†). Comparison of the two isomers, **6a** and **6a-iso**, demonstrates some differences in the occupancy of their HOMOs. In the case of **6a**, better planarity and consequently increased conjugation between the pyridine and fluorene rings, results in increased population on the central fluorene ring, whereas for the isomer **6a-iso** the HOMO is more delocalised over the molecule even extending onto the terminal alkoxyphenyl moieties (Fig. 1).

The most interesting feature of the electronic structure of the new compounds 6 and 7, compared to their benzene analogues 8 and 9, is the difference in the frontier orbital energies (Fig. 2). Whereas the HOMO energies for both series of compounds are almost the same (the difference is only  $\approx 0.03$ -0.04 eV), a pronounced decrease in the LUMO energies by 0.28 eV is observed when the benzene rings in 8a and 9a are replaced by pyridine rings (6a and 7a) (Fig. 2). Substitution of the phenyl rings in 8a and 9a by isomeric pyridine rings (compounds 6a-iso and 7a-iso) results in a decrease in HOMO energy levels by 0.14 eV (in contrast to 6a and 7a) whereas the decrease in their LUMO energies is less pronounced (0.19 eV), so the isomers 6a-iso and 7a-iso are expected to be weaker electron acceptors than 6a and 7a (although still stronger acceptors compared to 8 and  $9^{1/b}$ ). Similar results were obtained from the comparative orbital analysis of compounds 6a, 7a, 8a and 9a at the B3LYP/6-31G(d) level of theory (very similar HOMO orbital energies and a decrease in LUMO energies upon replacing the benzene rings by pyridine rings; see Fig. S3 in ESI<sup>†</sup>). This pronounced decrease in LUMO orbital energies in compounds 6a and 7a originates from the electron-deficient character of the pyridine rings and their orientation with respect to the fluorene moiety;



Fig. 2 B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) orbital energy level diagrams for compounds **6a**, **7a** and their comparison with isomers **6a-iso** and **7a-iso**, and benzene analogues **8a** and **9a**.



Fig. 3 Normalised UV–Vis absorption and photoluminescence spectra of compounds 8, 6 and 11 in dichloromethane.

this makes them stronger electron acceptors and on this basis increased ET properties and improved performance of OLEDs would be expected from compounds **6** and **7**.



Fig. 4 Current density *versus* electric field and light output *versus* electric field characteristics for MEH–PPV polymer blend OLEDs incorporating **6**, **7**, **8** and **9**. The polymer blends each contain 70% by weight of the electron transport materials. Device configuration: ITO/MEH–PPV : ETHB/A1.



Fig. 5 The external quantum efficiencies of MEH–PPV polymer blend OLEDs incorporating 70% by weight of 6, 7, 8 and 9. Device configuration: ITO/MEH–PPV : ETHB/Al.

#### Optoelectronic properties and device performance

The UV–Vis absorption and photoluminescence spectra in dichloromethane (Fig. 3) show an incremental red shift along the series 8, 6, 11 (Abs:  $356 \rightarrow 372 \rightarrow 394$  nm; PL:  $401 \rightarrow 411 \rightarrow 439$  nm), *i.e.* as the benzene rings are replaced by pyridines and thiophenes, consistent with a consecutive lowering of the HOMO–LUMO gap.

The current versus voltage (I–V) and light output versus voltage (L–V) characteristics of single-layer polymer blend devices using 6, 7, 8 and 9 are shown in Fig. 4 (positive bias applied to the ITO electrode). The device configuration was ITO/MEH–PPV : ETHB/AI and the polymer blends all contained 70% of the electron transport materials by weight. While the current density was similar for all the devices investigated, the electroluminescent output varied considerably. The light outputs from the new derivatives 6 and 7 were significantly higher than for the previously studied compounds 8 and 9. For example, at  $10 \times 10^5$  V cm<sup>-1</sup>, the light emission from blended devices containing 6 and 7 was about 2.5 times higher and 10 times higher, respectively, than from the device incorporating 8.

Fig. 5 shows the external quantum efficiencies of the OLEDs (data calculated from the optoelectronic characteristics of Fig. 4). The efficiency of devices based on 70% blends of **6** and **7** was *ca.* 0.08% and 0.25%, respectively. In comparison, the efficiency of blend devices incorporating 70% of **8** and **9** was *ca.* 0.05%, while that of a pure MEH–PPV reference device was  $10^{-3}$ %, and for OLEDs based on pure **7** less than  $10^{-3}$ %. The increase of the external quantum efficiency of an OLED can result from either an increase in the light emission or a decrease in the current (or both). From Fig. 4, it is evident that the improvement in the efficiencies of the devices containing **6** and **7** is due to increased light emission. This can almost certainly be attributed to an enhanced electron (minority carrier) injection from the top aluminium cathode.

The variation of quantum efficiency with the blend composition is depicted in Fig. 6. While the efficiency for



**Fig. 6** External quantum efficiency of blended MEH–PPV OLEDs incorporating **6**, **7** and **8**. Data are shown for blend devices with 50%, 70%, and 95% by weight.

8-containing OLEDs increased with concentration over the range of composition investigated, the efficiencies of devices incorporating compounds 6 and 7 appeared to saturate (in the case of 6) or even reduce (7) for devices containing high concentrations of the ET materials. The diminished efficiency of OLEDs containing compound 7 is probably related to a decrease in the light emission at high concentrations (95%) as the hole current is expected to reduce for blends consisting predominantly of the ET compound. The maximum external quantum efficiency that could be achieved from the blendedlayer devices was 0.24% for the OLED containing 70% of compound 7. This efficiency is over 200 times higher than that for pure MEH-PPV devices and about twice the highest values achieved with blended-layer devices incorporating 2,5-diphenyl-1,3,4-oxadiazole–fluorene hybrids 8 and 9.6 It is also significant that the 7 blended-layer devices were more efficient than OLEDs incorporating compound 6 throughout the concentration range investigated. There are other examples in the literature where the spiro-bifluorene system enhances efficiency compared to the 9,9-dialkylfluorene analogues which can yield fluorenone defects which quench the emission.<sup>15</sup>

The external quantum efficiency of our OLEDs could be increased further by using a layer of poly(3,4-ethylenedioxy-thiophene) doped with poly(styrenesulfonate) (PEDOT : PSS) between the ITO and the blended-layer film.<sup>17</sup> This resulted in an efficiency increase of 2–3 times, regardless of the composition and material. A 70% compound 7-containing blend device with PEDOT exhibited an external quantum efficiency of 0.5% and a luminous efficiency of 0.93 cd  $A^{-1}$  at 9.5 V and a luminance of 100 cd m<sup>-2</sup>. When the Al cathode was replaced by Ca/Al (thermally evaporated), the efficiency values for the 70% 7-based device increased further to 0.6% and 1.2 cd  $A^{-1}$  at 10.5 V.

The above result is interesting as the use of Ca increases significantly the efficiency with pure MEH–PPV (at 5 V and 100 cd m<sup>-2</sup> the EQE and the luminous efficiency for an ITO/ PEDOT/MEH–PPV/Ca/Al device were 0.42% and 0.72 cd A<sup>-1</sup>, respectively). However, only a very modest increase was



Fig. 7 The EL spectra of a pure MEH–PPV OLED and blendedlayer devices incorporating compounds 50% 8, 70% 6, and 50% 7 by weight.

observed for our blends. This suggests that the two methods of enhancing the electron injection into the emissive polymer are mutually exclusive, *i.e.* one can either use a low work function metal such as Ca, or exploit a blended-layer structure containing an electron transporting component. For the latter devices, it appears that there is not much further gain in then adding Ca as a top electrode. Indeed, for the systems studied in our work the use of blended layers with an Al cathode offers a distinct advantage in terms of environmental stability and ease of handling as Ca electrodes are highly reactive and unstable in the atmosphere. Previous workers noted no significant improvement in EL efficiency by replacing Al with Ca for an emissive poly(p-phenylenevinylene) derivative with a pendant 1,3,4-oxadiazole substituent.<sup>18</sup> Prior to our work it was not clear that blended layer devices comprising materials with very different molecular weights would achieve the same result.

Fig. 7 contrasts the EL spectrum of a pure MEH-PPV device with the spectra from 50% 8, 50% 7 and 70% 6 blendedlayer OLEDs. The emission from all these devices was from MEH-PPV. No EL could be detected from the ET materials, which are all blue emitters. The pure MEH-PPV device exhibited a main peak at 570 nm while the spectra of the blended-layer devices were red-shifted, with the main peaks located at ca. 590 nm. Devices incorporating 9 also showed a similar red-shifted EL spectrum (data not shown). All these materials possess C12H25O groups at both ends of the molecules. It is believed that these long terminal groups are responsible for the red shift, as the EL spectrum from a blended-layer device incorporating a compound with the same molecular structure as 8, but no long hydrocarbon end groups, did not show the red-shift.<sup>7b</sup> It is known that the emission of conjugated polymers such as MEH-PPV can be changed by varying its chain conformation. This, in turn, is affected by the polarity of the solvent or by the spin casting speed.<sup>19,20</sup>

The implication of this work and of our previous studies<sup>7</sup> is that the components of the blended layers (polymer and ET material) are intimately mixed. The fact that no direct EL from the ET materials could be measured, even at high concentration (up to 95%), implies that the molecules of these materials are well-distributed among the MEH–PPV polymer chains.



**Fig. 8** AFM images of the 70% **6** (a) and 50% **7** (b) blend films spin-cast from the blend solution using chloroform as the solvent; 50% **6** (c) and 50% **7** (d) blend films from the blend solutions using the mixture of chloroform and *p*-xylene (3 : 1 v/v).

Under certain conditions, however, we found that phase separation could be observed for blended-layer devices based on 6 and 7; for example, by using films that were spin-cast from solutions of a mixed solvent. Fig. 8 shows atomic force microscope images of 70% 6 (a) and 50% 7 (b) blended-layer films spin-cast from the mixed solution using chloroform as the solvent; and 50% 6 (c) and 50% 7 (d) films formed using a mixed solvent system, *viz.* chloroform and *p*-xylene (3:1 v/v). There is no notable morphology in the blend films spin-coated from the pure chloroform solution (the micron-size particles evident in Figs. 8a and 8b are thought to originate from environmental contamination during processing). However, a needle-like phase is clearly visible in both the blended-layer films formed from the mixed solvent. The phase separation was particularly acute in the films containing compound 7. This is probably related to the presence of the bulky spiro unit at the centre of the molecule, which inhibits mixing with the chains of the MEH-PPV. (This solvent effect was not observed in comparable experiments using ET materials 8 and 9). The microstructure and crystallinity of MEH-PPV films are known to vary depending on the solvents from which the film has been cast.<sup>21</sup>

In contrast to the results presented earlier (Fig. 7), EL from the ET compounds was evident in OLEDs incorporating phase-separated layers. Fig. 9 compares the EL spectra of a 70% 7 blended-layer device formed from pure chloroform with 70% 6 and 70% 7 blended-layer devices formed using the mixed solvent. Small shoulders in the 420–520 nm region can be seen in the spectra for the OLEDs fabricated using the mixed solvent; this is more evident for the device containing

compound 7. These peaks coincide with the emission from devices based on the pure ET compounds 6 and 7. The phase separation also affected the external quantum efficiencies of the devices. The efficiency of all these devices decreased as the blend composition exceeded 50% of the ET material and was less than 0.1%. The interface between the separated phase and the matrix can act as a quenching site where non-radiative singlet-exciton decay takes place, consequently reducing the light emission and the efficiency. Another reason for the efficiency decrease with the concentration can be that more light will be emitted from clusters of 7.



Fig. 9 The EL spectra of 70% 7 devices spin-cast from chloroform solution; 70% 6 and 7 device from the solution using a mixture of chloroform (CF) and p-xylene (Xy) solvent.

## Conclusions

We have synthesised the first 2,5-diaryl-1,3,4-oxadiazolefluorene hybrids which incorporate pyridine units within the linearly-extended  $\pi$ -electron system, viz. 2,7-bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2-pyridyl}-9,9-dihexylfluorene (6) and 2,7-bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2-pyridyl}spirobifluorene (7). Calculations at the DFT level establish that inclusion of the pyridyl rings in 6 and 7 considerably enhances the electron affinity of the system, compared to regioisomers and phenyl analogues. Single-layer OLEDs were fabricated by spin-coating blends of MEH-PPV as the emissive material with added ET compounds 6 or 7. The external quantum efficiencies of the devices were greatly enhanced compared to pure MEH-PPV reference devices. The EQE for the device ITO/PEDOT : PSS/MEH-PPV-7 (30: 70% by weight)/Al reached 0.5% and a luminous efficiency of 1.1 cd  $A^{-1}$  at 11 V and a luminance of 100 cd  $m^{-2}$ . Replacing the Al cathode with Ca/Al gave only a modest increase in efficiency (EQE 0.6% and  $1.3 \text{ cd } \text{A}^{-1}$  at 9.3 V) unlike the pure MEH-PPV reference device where a far greater increase in efficiency occurs. This leads to the important conclusion that electron injection into the MEH-PPV emitter can be enhanced either by using a low work function metal such as Ca, or by exploiting a blended-layer structure. There are important practical implications in this discovery, as if comparable device performance can be achieved, it is preferable to use Al electrodes rather than Ca electrodes: the latter are highly reactive and are unstable in the atmosphere. Further work which exploits the advantages of blended-layer devices is in progress.

## Experimental

## General

The procedures and equipment used for the synthesis and characterisation of materials are the same as those reported recently.<sup>7</sup>

## Device fabrication and measurement

MEH-PPV was purchased from Aldrich whereas the ET materials were synthesised as described below. Indium-tinoxide (ITO) coated glass from Merck with sheet resistance of 9  $\Omega$   $\Box^{-1}$  was used as the anode. This was cleaned by ultrasonication in acetone and isopropyl alcohol for 30 min each and dried with a nitrogen gun. The polymer and ET materials were dissolved in chloroform or in a mixture of chloroform and p-xylene (3 : 1 v/v) to provide the blend solution, which was spin-coated onto the ITO. The concentration of ET material was changed from 50% to 95% of the total weight. Following the spin-coating, Al or Ca/Al top electrodes, in the form of dots (radius 1 mm; thickness 150 nm) were thermally evaporated at a pressure of about  $10^{-6}$  mbar. In some cases PEDOT : PSS, purchased from Bayer AG, was spin-coated onto the ITO prior to the deposition of the polymer blend. These PEDOT layers (40 nm in thickness) were dried for 12 h in nitrogen at room temperature to remove residual solvent.

Electrical measurements were undertaken in a vacuum chamber  $(10^{-1} \text{ mbar})$ . The d.c. bias was applied and the current measured by a Keithley 2400 Source Meter. The light emitted from the device was collected by a large area photodiode (1.5 cm diameter) connected to a Keithley 485 Digital Picoammeter. For external quantum efficiency measurements, the light power was calculated using the photocurrent and the conversion factor (wavelength dependent) of the photodiode (ampere/watt). Electroluminescence (EL) spectra were measured using an Ocean Optics USB2000 Miniature Fibre Optic Spectrometer. The surface morphologies of the blend films were observed using a Digital Instrument NanoScope E atomic force microscope.

## **Computational procedures**

The ab initio computations for compounds 6a, 7a, 6a-iso, and 7a-iso were carried out with the Gaussian 03<sup>22</sup> package of programs at density-functional theory (DFT) level. The geometries were optimised using Pople's 6-31G split valence basis set supplemented by d-polarisation functions on heavy atoms. In the DFT calculations, Becke's three-parameter hybrid exchange functional<sup>23</sup> with Lee-Yang-Parr gradientcorrected correlation functional (B3LYP)<sup>24</sup> was employed. No symmetry restrictions and no constraints of bonds/angles/ dihedral angles were applied and all atoms were free to optimise. For the B3LYP/6-31G(d) optimised geometries, electronic structures were then calculated for single points using a triple split-valence 6-311 basis set supplemented by two d-polarisation functions on heavy atoms and p-polarisation functions on hydrogens [B3LYP/6-311G(2d,p)]. Contours of HOMO and LUMO orbitals were visualised using the Molekel v.4.3 program.<sup>25</sup>

## 6-Bromonicotinic acid (1)

2-Bromo-5-methylpyridine (17.2 g, 100 mmol) and phase transfer agent Aliquat-336 (0.5 cm<sup>3</sup>) in water (350 cm<sup>3</sup>) were heated at 70 °C. Powdered KMnO<sub>4</sub> (44 g, 0.28 mol) was added carefully in small potions over a period of 3 h. The mixture was then refluxed for a further 1.5 h. After cooling, the solid was filtered off, washed with hot water and the combined filtrates were concentrated to *ca*. 150 cm<sup>3</sup>, then acidified with HBr (48%) and cooled in an ice bath. The precipitate was then filtered off, washed with water, recrystallised from water and dried to yield **1** as colourless plates (10.1 g, 50%), mp 194.5–195.0 °C (lit.<sup>11</sup> 195 °C). Anal. Calcd. for C<sub>6</sub>H<sub>4</sub>BrNO<sub>2</sub>: C, 35.67; H, 2.00; N, 6.93. Found: C, 35.61; H, 1.99; N, 6.95%.  $\delta_{\rm H}$  (DMSO-d<sub>6</sub>, 400 MHz) 8.87 (d, *J* 2, 1H), 8.16 (dd, *J*<sub>ab</sub> 8.2, *J*<sub>ac</sub> 2, 1H), 7.80 (d, *J* 8.2, 1H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 100 MHz) 165.51, 151.12, 145.54, 139.86, 128.23, 126.42.

# 2[5-(2-Bromopyridyl)]-5-(4-dodecyloxyphenyl)-1,3,4-oxadiazole (3)

6-Bromonicotinic acid 1 (6.6 g, 32.7 mmol) was refluxed in thionyl chloride (40 cm<sup>3</sup>) for 12 h under nitrogen. The excess thionyl chloride was then removed by vacuum distillation. Dry toluene (30 cm<sup>3</sup>) was then added and distilled off at reduced pressure to remove any remaining thionyl chloride. After

cooling to rt, 4-dodecyloxybenzoic acid hydrazide  $2^{26}(10.58 \text{ g})$ 33 mmol) dissolved in pyridine (50 cm<sup>3</sup>) was added via a syringe. The solution was stirred for 1 h at rt and then for a further 2 h at 110 °C. Pyridine was removed by vacuum distillation. After cooling to rt, methanol (50 cm<sup>3</sup>) was then added and the suspension was heated at reflux for 15 min, cooled and a solid obtained by vacuum filtration. The crude intermediate product was dried for 12 h under high vacuum and then refluxed with phosphorus oxychloride (40 cm<sup>3</sup>) for 12 h after which time the POCl<sub>3</sub> was removed by vacuum distillation yielding a cream solid. Methanol (50 cm<sup>3</sup>) was then added and the suspension was heated at reflux for 15 min, cooled and the solid obtained by vacuum filtration. The crude product was dried for 12 h under high vacuum and then dissolved in a minimum amount of dichloromethane. HBr (in glacial acetic acid, 33%) (20 cm<sup>3</sup>) was then added and the suspension was stirred at rt for 96 h. The suspension was then diluted with  $H_2O$  (20 cm<sup>3</sup>) and neutralised with  $Na_2CO_3$  (2 M). The mixture was extracted with dichloromethane, washed with NaOH and then H<sub>2</sub>O and filtered through celite before drying with MgSO<sub>4</sub> and filtering. The solution was concentrated in vacuo and the crude product was then purified by column chromatography (silica, eluent: CHCl3-EtOAc 19:1 v/v) and crystallisation (ethanol) to yield white crystals of compound 3 (5.9 g, 37%), mp 144-144.5 °C. MS (EI) m/z 487 (M<sup>+</sup>, <sup>81</sup>Br), 485 (M<sup>+</sup>, <sup>79</sup>Br). Anal. Calcd for C<sub>25</sub>H<sub>32</sub>BrN<sub>3</sub>O<sub>2</sub>: C, 61.73; H, 6.63; N, 8.64. Found: C, 61.58; H, 6.63; N, 8.43%.  $\delta_{\rm H}$ (CDCl<sub>3</sub>, 400 MHz) 9.08 (d, J 2.4, 1H), 8.28 (dd, J<sub>ab</sub> 8.4, J<sub>ab</sub> 2.4, 1H), 8.07 (d, J 8.8, 2H), 7.69 (d, J 8.4, 1H), 7.04 (d, J 8.8, 2H), 4.05 (t, J 6.8, 2H), 1.83 (m, 2H), 1.28 (m, 18H), 0.89 (t, J 6, 3H),  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 100 MHz) 165.30, 162.40, 160.00, 154.21, 147.68, 136.50, 128.89, 128.54, 119.63, 115.50, 115.14, 68.38, 31.91, 29.64, 29.62, 29.58, 29.55, 29.35, 29.33, 29.11, 25.99, 22.67, 14.09.

#### General procedure for the cross-coupling reactions

The diboronic acid or boronate reagent, the halide and the catalyst [tetrakis(triphenylphosphino)palladium] (5 mol % relative to the boronic acid) were added sequentially to degassed THF or toluene and the mixture was stirred at 20 °C for 0.5 h. Degassed aqueous Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> solution was added and the reaction mixture was heated under argon (oil bath temperature 80 °C) until TLC monitoring showed that the reaction was complete. Solvent was evaporated *in vacuo* and the crude products were extracted into organic solvent. The organic layer was washed with H<sub>2</sub>O, separated and dried over MgSO<sub>4</sub>. Products were purified by column chromatography.

## 2,7-Bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2pyridyl}-9,9-dihexylfluorene (6)

Following the general procedure, compound **3** (0.196 g, 0.4 mmol), compound **4** (0.077 g, 0.18 mmol), tetrakis(triphenylphosphino)palladium (23 mg, 0.02 mmol), THF (25 cm<sup>3</sup>) and Na<sub>2</sub>CO<sub>3</sub> (2 M, 0.6 cm<sup>3</sup>); reaction time 48 h; extracted with DCM. Chromatography eluent: DCM–EtOAc (19 : 1 v/v) followed by a further column, eluent: DCM–EtOAc (9 : 1 v/v) and recrystallisation from ethanol gave **6** as a white solid

(0.073 g, 35%), mp 166.7–167.5 °C. MS (MALDI-TOF) *m/z* Calcd. for C<sub>75</sub>H<sub>96</sub>N<sub>6</sub>O<sub>4</sub>: 1145.76. Found 1145.73 (M<sup>+</sup>); Anal. Calcd. for C<sub>75</sub>H<sub>96</sub>N<sub>6</sub>O<sub>4</sub>: C, 78.63; H, 8.45; N, 7.34. Found: C, 78.99; H, 8.51; N, 6.94%.  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 400 MHz) 9.44 (d, *J* 2, 2H), 8.51 (dd, *J*<sub>ab</sub> 8, *J*<sub>ac</sub> 2, 2H), 8.14 (m, 4H), 8.12 (d, *J* 8.8, 4H), 8.02 (d, *J* 8, 2H), 7.9 (d, *J* 8, 2H), 7.06 (d, *J* 8.8, 4H), 4.06 (t, *J* 6.4, 4H), 2.17 (m, 4H), 1.84 (m, 4H), 1.5–1.3 (m, 36H), 1.1 (m, 12H), 0.9 (t, *J* 6.4, 6H), 0.74 (m, 10H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 100 MHz) 165.02, 162.25, 159.81, 152.33, 147.66, 142.40, 134.80, 134.78, 128.84, 126.43, 121.59, 120.64, 120.44, 120.41, 118.62, 115.86, 115.12, 68.37, 55.70, 53.39, 40.38, 31.91, 31.50, 29.65, 29.63, 29.59, 29.56, 29.37, 29.34, 29.13, 26.00, 23.88, 22.68, 22.56, 14.10, 13.95. UV–Vis (DCM)  $\lambda_{\rm max}$  372 nm, PL (DCM)  $\lambda_{\rm max}$  411, 431 nm.

## 2,7-Bis{5-[2-(4-dodecyloxyphenyl)-1,3,4-oxadiazol-5-yl]-2pyridyl}spirobifluorene (7)

Compound 3 (0.486 g, 1 mmol), compound 5 (0.284 g, 0.5 mmol), tetrakis(triphenylphosphino)palladium (58 mg, 0.05 mmol), tri-tert-butylphosphine (0.02 g, 0.1 mmol), toluene  $(20 \text{ cm}^3)$  and  $K_2CO_3$  (2 M, 2.5 cm<sup>3</sup>); reaction time 48 h; extracted with chloroform. Chromatography eluent: CHCl3-EtOAc (17 : 3 v/v) followed by recrystallisation from a toluene-ethanol mixture gave compound 7 as a yellow solid (0.32 g, 56%), mp 203.0-203.4 °C. MS (MALDI-TOF) m/z Calcd. for  $C_{75}H_{78}N_6O_4$ : 1127.62. Found 1127.65 (M<sup>+</sup>); Anal. calcd. for C75H78N6O4: C, 79.90; H, 6.97; N, 7.45. Found: C, 79.70; H, 7.00; N, 7.26%.  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 400 MHz) 9.27 (s, 2H), 8.33 (d, J 8.4, 2H), 8.23 (d, J 8, 2H), 8.04 (m, 6H), 7.94 (d, J 8, 2H), 7.72 (d, J 8.4, 2H), 7.43 (m, 4H), 7.15 (t, J 7.6, 2H), 7.02 (d, J 8.4, 4H), 6.84 (d, J 7.6, 2H), 4.04 (t, J 6, 4H), 1.82 (m, 4H), 1.5–1.3 (m, 36H), 0.89 (t, J 6.4, 6H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 100 MHz) 164.95, 162.19, 162.09, 159.13, 150.4, 147.98, 147.45, 142.85, 142.0, 138.30, 134.57, 128.81, 128.10, 127.48, 127.17, 124.25, 122.72, 121.00, 120.43, 120.30, 118.62, 115.76, 115.06, 68.33, 66.15, 31.92, 29.66, 29.64, 29.59, 29.57, 29.39, 29.37, 29.12, 25.99, 22.70, 14.13. UV–Vis (DCM) λ<sub>max</sub> 371 nm, PL (DCM) λ<sub>max</sub> 407, 430 nm.

## 2,7-Bis{5-[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]-thien-2-yl}-9,9-dihexylfluorene (11)

By analogy with the synthesis of 6, compound 10 (0.3 g)0.73 mmol), compound 4 (0.17 g, 0.40 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (29 mg, 0.04 mmol), tri-tert-butylphosphine (0.01 cm<sup>3</sup>, 0.1 mmol), THF (50 cm<sup>3</sup>) and Na<sub>2</sub>CO<sub>3</sub> (2 M, 1.0 cm<sup>3</sup>); reaction time 96 h; extracted with toluene. Chromatography eluent: DCM-EtOAc (32.3 : 1 v/v) followed by DCM-EtOAc (9:1 v/v) and recrystallisation from toluene-ethanol gave yellow needles of 11 (0.15 g, 42%), mp 252.6-253.0 °C. MS (EI) m/z 898 (M<sup>+</sup>, 100%). Anal. calcd. for C<sub>57</sub>H<sub>62</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 76.13; H, 6.95; N, 6.23. Found: C, 75.73; H, 6.89; N, 5.91%.  $\delta_{\rm H}$ (CDCl<sub>3</sub>, 400 MHz) 8.08 (d, J 8.4, 4H), 7.84 (d, J 4, 2H), 7.78 (d, J 8.0, 2H), 6.70 (d, J 8.0, 2H), 7.65 (s, 2H), 7.57 (d, J 8.4, 4H), 7.47 (d, J 4, 2H), 2.07 (m, 4H), 1.40 (s, 18H), 1.11 (m, 12H), 0.77 (m, 10H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 100 MHz) 164.12, 160.93, 155.43, 152.16, 149.75, 141.11, 132.39, 130.54, 128.81, 126.08, 125.34, 123.85, 123.75, 120.94, 120.61, 120.41, 55.53, 40.35,

35.12, 31.43, 31.13, 29.62, 23.79, 22.54, 13.96. UV–Vis (DCM)  $\lambda_{max}$  394 nm, PL (DCM)  $\lambda_{max}$  439, 466 nm.

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