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Synthesis and device characterisation of side-chain polymer electron transport materials for organic semiconductor applications

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Improved syntheses and polymerisations are reported of monomers bearing electron transporting substituents based on 2,5-diphenyloxadiazole and 2,3-diphenylquinoxaline attached directly to a vinyl group. By copolymerisation and by use of mixtures of homopolymers, these materials have been incorporated into light emitting polymer devices in which hole conduction properties are provided by 4-vinyltriphenylamine groups. High luminescence efficiency is achieved by use of a fluorescent additive. The resulting devices show narrow emission bands and high brightnesses, except in the case of those based on a diphenyloxadiazole–triphenylamine polymer blend. Thermal analysis data are equivocal but we present evidence that in this system, but not the quinoxaline blend, phase separation occurs. The minority charge carrying capacity of the homopolymers is probed: it is shown that the quinoxaline derivative has hole blocking properties superior to those of the oxadiazole polymer and is a good candidate for use in optimised devices.

1 Introduction

Light emitting devices based on conjugated polymers or evaporated thin films of molecular semiconductors have achieved prominence as candidates for a new generation of flat panel emissive displays and lighting elements.[1,2] For each of these approaches a capability to achieve useful brightness, colour range and operating lifetime has been demonstrated. The use of sidechain polymers as charge transport materials in organic light emitting devices has been relatively underexplored, despite their use[3] in early work on the subject and the widespread application of poly(vinylcarbazole) in electrophotographic printers and copiers. Recently, interesting results on this class of materials have been reported by several groups,[4–8] but the level of activity remains much lower than that on either conjugated mainchain polymers or low molecular mass components. Two factors give rise to our interest in sidechain systems. Firstly, the isolation of the electronically active sidegroups from one another permits relatively simple molecular engineering, directly comparable to that used in low molar mass materials. As a consequence we expect that properties such as the carrier injection potentials, mobilities and emission wavelengths of pendant groups in sidechain polymers will be easily varied and controlled. On the other hand, the use of polymeric materials allows rapid, easy and cost effective processing of the thin layers required in devices.

Studies of charge transport by molecular semiconductors dispersed in an electronically inert polymer host have demonstrated an exponential decrease in carrier mobility as the concentration of charge transport species is reduced. Thus, in order to achieve the highest possible carrier mobility, it is desirable that the electronically inert polymer backbone should comprise as small a fraction of the material as possible. For this reason we have concentrated on materials in which a vinyl group is directly substituted onto the charge carrying aromatic moiety.

This paper reports a comparison of devices based on electron transport materials derived respectively from oxadiazole and quinoxaline substituted vinylic polymers, either as homopolymers or as copolymers with the hole transport material poly(4-vinyltriphenylamine), PVTPA.[9] Oxadiazole derivatives have been explored as electron transport materials, in the form of evaporated molecular films,[10] and as structural components of conjugated polymers,[11] jointed rod mainchain polymers[12] and sidechain polymethacrylates.[13,14] Quinoxalines have attracted relatively less attention, but have been studied as components of conjugated polymers,[15] as dimers[16] and as starburst oligomers.[17] In the devices reported here, both electron and hole transport properties are present in a single organic layer. Such devices usually show lower efficiency than heterojunction structures in which hole and electron transport functions are separated, both because of the reduction in mobility of each charge carrier, and because of the possibility of charge carriers of either sign traversing the device without recombination and light emission taking place.

2 Experimental

2.1 Polymer preparation

The polymers considered in this work are shown in Fig. 1. Our attempts to repeat the synthesis of 2-(4-vinylphenyl)-5-phenyloxadiazole (4VPPO) according to the literature route[18] gave low yields, so a modified route was developed (Scheme 1) and also applied to the synthesis of 2-(3-vinylphenyl)-5-phenyloxadiazole. Reaction of 3-bromobenzoyl chloride with 5-phenyl-1H-tetrazole gave good yields of 2-(3-bromophenyl)-5-phenyloxadiazole. Generation of the corresponding Grignard reagent proved difficult, but vinylation of the compound *via* Pd^0 mediated coupling of the aryl bromide with tributylvinyltin worked well.

The preferred synthesis route for 6-vinyldiphenylquinoxaline is shown in Scheme 2. Condensation of benzil with 1,2-diamino-4-methylbenzene provided 6-methyl-2,3-diphenylquinoxaline in good yield. Selective bromination of the methyl group with NBS was followed by a Wittig reaction with

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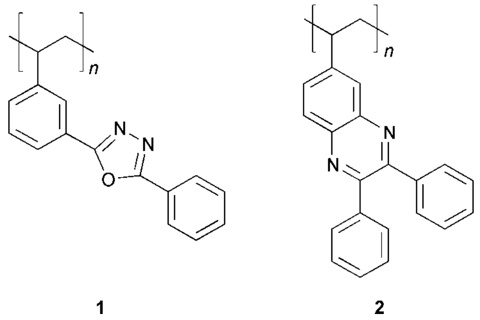


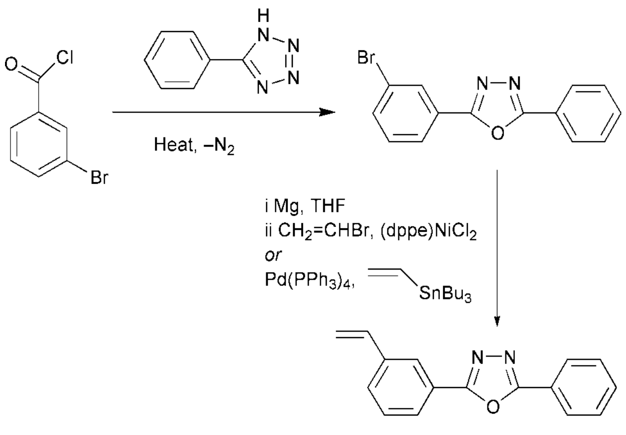
Fig. 1 Chemical structures of electron transporting sidechain polymers.

methanal to yield the 6-vinyl product. This route afforded a product that was more easily purified than alternative routes involving coupling of 6-haloquinoxalines with vinyl metal reagents.

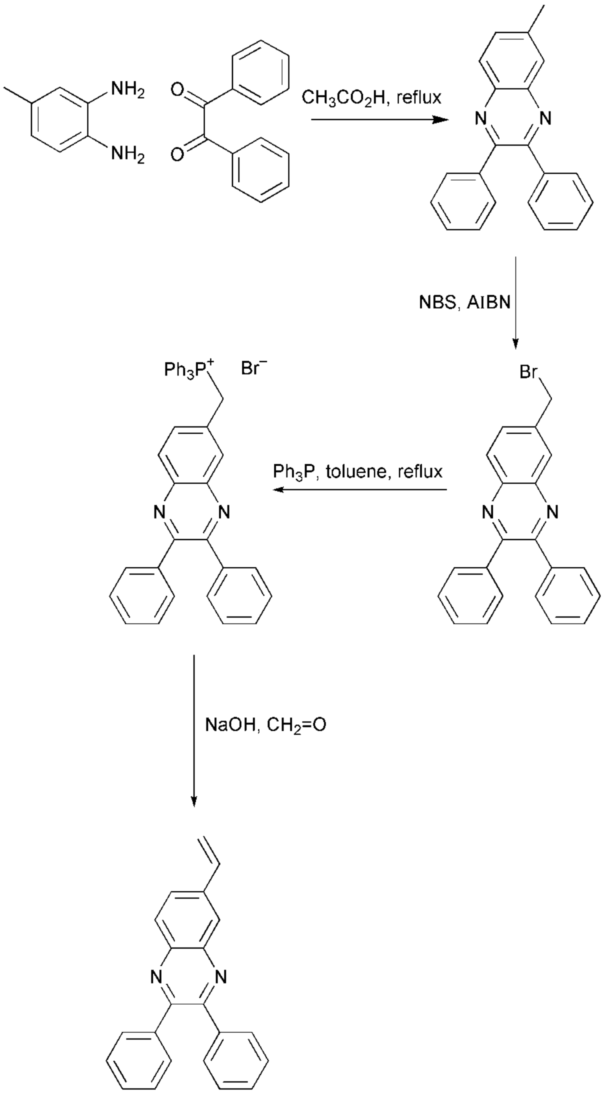
All of the monomers were readily polymerised under free radical conditions using 2% AIBN under nitrogen in benzene at 70 °C. The product polymer was recovered by precipitation into an excess of non-solvent and dried under vacuum. Poly-4-vinyltriphenylamine was prepared as previously described.[9]

Characterisation data for the homopolymers are set out in Table 1 together with the properties of random copolymers obtained by polymerisation of 1 : 1 mole ratios of the respective monomers under the same conditions used for the homopolymer syntheses. The mole ratios of the monomers incorporated in each product were estimated from the intensity ratios of peaks in the ^{1}H NMR spectra associated with each repeat unit. As noted in Table 1, copolymerisation of VTPA and VDPQ gave essentially a 1 : 1 incorporation of the two monomers in the product polymer. The starting solution of the VTPA and VDPQ monomers, and that of the resultant copolymer, was yellow which we attribute to the formation of a charge transfer complex between the two charge carrying units. Copolymerisation of VTPA with 3-VPPO, gave a higher degree of incorporation of the oxadiazole in the product than was the case with VDPQ indicating the higher reactivity of the former monomer.

Synthesis of 2-(3-bromophenyl)-5-phenyl-1,3,4-oxadiazole. 5-Phenyltetrazole (6.7 g, 45.5 mmol), 3-bromobenzoyl chloride (10.0 g, 45.5 mmol) and toluene (250 ml) were refluxed overnight to give a clear yellow solution. Upon cooling a small amount of white solid formed which was removed by filtration. This proved not to be an oxadiazole. The remaining solution was evaporated and the residual solid recrystallised from methanol to give fine crystals of 2-(3-bromophenyl)-5-phenyl-1,3,4-oxadiazole (10.5 g, 76%. Found C, 77.22; H, 4.84; N, 11.21%. $C_{14}H_{15}N_2OBr$ requires C, 77.4; H, 4.87; N, 11.28%).



Scheme 1 Synthesis of 2-(3-vinylphenyl)-5-phenyloxadiazole.



Scheme 2 Synthesis of 6-vinyl-2,3-diphenylquinoxaline.

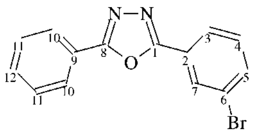
^{1}H NMR ($CDCl_3$, 300 MHz). δ ppm 8.28 (q, $^4J_{HH}$ 1.7 Hz, 1H, H7), 8.12–8.18 (m, 2H, H10 or H11), 8.09 (dq, $^3J_{HH}$ 9.0 Hz, $^4J_{HH}$ 0.9 Hz, 1H, H5), 7.68 (dm, $^3J_{HH}$ 9 Hz, 1H, H3), 7.5–7.6 (m, 3H, H10 or H11, and H12), 7.42 (td, $^3J_{HH}$ 8.1 Hz, $^5J_{HH}$ 1.5 Hz, 1H, H4)

^{13}C NMR ($CDCl_3$, 75 MHz). δ ppm 165.12 and 163.51 (C8 and C1), 134.89 (Aromatic C), 132.19 (Aromatic C), 130.89 (Aromatic C), 129.96 (Aromatic C), 129.36 (C11 or C10), 127.25 (C11 or C10), 126.00 (C6), 125.69 (Aromatic C), 128.87 and 123.34 (C2 and C9).

Table 1 Properties of polymers synthesised

Polymer	M_n, M_w	PDI	T_g/°C	Monomer Ratio
P3VPPO	20000, 47100	2.35	144	—
PVDPQ	12900, 39000	3.0	205	—
PVTPA	9300, 55000	5.9	146	—
PVTPA : P3VPPO	9700, 19400	2.0	132	~1 : 1.9
PVTPA : PVDPQ	11500, 57500	5.0	173	~1 : 1

Melting point. 127–128 °C (lit.[19] 125–126 °C).



Synthesis of 2-(3-vinylphenyl)-5-phenyl-1,3,4-oxadiazole. 2-(3-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (2.0 g, 6.64 mmol) was dissolved in degassed toluene (30 ml). $Pd(PPh_3)_4$ (0.15 g, 0.133 mmol) and $^nBu_3Sn(CHCH_2)$ (2.11 g, 6.64 mmol) were added under dry nitrogen. The solution was refluxed for 4 hours after which time a ^1H NMR spectrum of a sample of the solution showed total consumption of the starting materials. The solution was evaporated to give a yellow solid which was recrystallised from hexane to give a yellow oil. This was redissolved in toluene and passed through a silica packed column giving a strong yellow band. The column was eluted with toluene until the yellow band reached the bottom of the column. The toluene collected was evaporated and shown to contain only $^nBu_3SnBr$. The column was stripped with methanol, the methanol evaporated and the residue recrystallised from hexane to give white crystals (0.9 g, 54%) which were shown by ^1H NMR to be 2-(3-vinylphenyl)-5-phenyl-1,3,4-oxadiazole with only traces of $^nBu_3SnBr$.

^1H NMR (CDCl3, 300 MHz). δ 8.1–8.2 (m, 3H, aromatic C*H*), 8.02 (dt, 1H, aromatic C*H*), 7.6–7.4 (m, 5H, aromatic C*H*), 6.80 (dd, $^3J_{HH}$ 17.7 Hz and 10.8 Hz, C*H*CH$_2$), 6.90 (d, $^3J_{HH}$ 17.7 Hz, CHC*H*$_2$), 5.39 (dd, $^3J_{HH}$ 0.8 Hz, CHC*H*$_2$).

Synthesis of 6-methyl-2,3-diphenylquinoxaline. 1,2-Diamino-4-methylbenzene (25.0 g, 0.20 mol) and benzil (43 g, 0.20 mol) were refluxed in ethanoic acid (250 ml) overnight. The solvent was evaporated *in vacuo* and the black residue recrystallised three times from ethanol to give pale brown crystals of 6-methyl-2,3-diphenylquinoxaline (39.6 g, 65%).

^1H NMR ($CDCl_3$, 300 MHz) δ 8.08 (d, *J* 8.4 Hz, 1H, Hs of quinoxaline), 7.97 (br s, 1H, Hs of quinoxaline), 7.60 (dd, *J* 8.4, *J* 1.8Hz, 1H, Hs of quinoxaline), 7.50–7.58 (m, 4H, phenyl rings), 7.30–7.38 (m, 6H, phenyl rings), 2.62 (s, 3H, C*H*$_3$).

Melting point. 114.5–116 °C (lit.[20] 115–116 °C).

Synthesis of 6-bromomethyl-2,3-diphenylquinoxaline. 6-Methyl-2,3-diphenylquinoxaline (5.0 g, 16.9 mmol) was dissolved in dry, oxygen free benzene (50 ml). The solution was brought to reflux and a mixture of NBS (3.00 g, 16.9 mmol) and AIBN (0.1 g) added as a solid over a period of 30 minutes. The solution was then refluxed for 2 h, cooled, washed with water (3 × 100 ml), dried over $MgSO_4$ and evaporated to leave a pale brown solid. This was recrystallised from hexane–toluene (1 : 1, 80 ml) to yield 6-bromomethyl-2,3-diphenylquinoxaline (3.5 g, 56%. Calc. for $C_{21}H_{15}N_2Br$ C, 67.21; H, 15.12; N, 7.47%. Found C, 67.17; H, 3.95; N, 7.41% despite the fact that traces of 6-methyl-2,3-diphenylquinoxaline were shown to be present by ^1H NMR).

^1H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, *J* 8.7 Hz, 1H, Hs of quinoxaline), 8.16 (d, *J* 2.2 Hz, 1H, Hs of quinoxaline), 7.78 (dd , *J* 8.7, *J* 2.2 Hz, 1H, Hs of quinoxaline), 7.48–7.56 (m, 4H, phenyl ring), 7.30–7.40 (m, 6H, phenyl ring), 4.71 (s, 2H, CH_2Br).

Synthesis of triphenyl(2,3-diphenylquinoxalinylmethyl)phosphonium bromide. 6-Bromomethyl-2,3-diphenylquinoxaline (1.0 g, 2.7 mmol) and triphenylphosphine (0.70 g, 2.7 mmol) were dissolved in toluene (50 ml) and the solution refluxed overnight. The white solid that precipitated was recovered by filtration and dried *in vacuo* to give triphenyl(2,3-diphenylquinoxalinylmethyl)phosphonium bromide (1.58 g, 93%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.1–7.8 (m, 29H, aromatic Hs), 5.82 (d, $^2J_{HP}$ 13 Hz, 2H, C*H*$_2$P).

Synthesis of 6-vinyl-2,3-diphenylquinoxaline. Triphenyl(diphenylquinoxalinylmethyl)phosphonium bromide (1.50 g, 2.35 mmol) was dissolved in dichloromethane (3 ml) and formaldehyde (0.40 ml, 37% solution in water, 4.7 mmol) added. Aqueous sodium hydroxide (1.5 ml, 50% solution) was added dropwise over a period of 30 minutes with rapid stirring and stirred for a further 30 minutes. The solution was diluted with dichloromethane, washed with water, dried over $MgSO_4$ and evaporated to dryness to give a pale yellow solid. This solid was purified by column chromatography on silica with hexane as the eluent to give white crystals, 10.5 g, 50% (mp 122–123 °C, lit.[21] 122–123 °C. Found C, 85.69; H, 5.19; N, 9.12%. $C_{22}H_{16}N_2$ requires C, 85.69; H, 5.23; N, 9.08%). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, $^3J_{HH}$ 8.7 Hz, 1H, quinoxaline H), 8.10 (br, 1H, quinoxaline H), 7.90 (dd, $^3J_{HH}$ 8.7 Hz, $^4J_{HH}$ 2.1 Hz, quinoxaline H), 7.45–7.55 (m, 4H, phenyl H), 7.28–7.38 (m, 6H, phenyl H), 6.95 (dd, $^3J_{HH}$(cis) 11.1 Hz, $^3J_{HH}$(trans) 17.7 Hz, 1H, vinylic H), 6.00 (d, $^3J_{HH}$(trans) 17.7 Hz, 1H, vinylic H), 5.47 (d, $^3J_{HH}$(cis) 11.1 Hz, 1H, vinylic H).

Copolymerisation of 4-vinyltriphenylamine with 2-phenyl-5-(3-vinylphenyl)-1,3,4-oxadiazole. 2-Phenyl-5-(3-vinylphenyl)-1,3,4-oxadiazole (0.60 g, 2.4 mmol), 4-vinyltriphenylamine (0.60 g, 2.2 mmol) and AIBN (19.71 mg, 120 µmol) were placed in an ampoule and benzene (5 ml) condensed into the ampoule under vacuum. The solution was then heated in the ampoule to 70 °C for 10 hours, cooled and the product poured into methanol (50 ml). The polymer which precipitated was collected by filtration and dried under vacuum to yield 0.80 g of a white powder.

GPC analysis ($CHCl_3$): $\bar{M}_n$ 15,700, $\bar{M}_w$ 53,000, $\bar{M}_w/\bar{M}_n$ /3.4 Other polymers were prepared from the corresponding monomers under the same conditions.

2.2 Organic device fabrication and test

The polymers under investigation are charge-transport materials with negligible emission properties. In order to assess their performance in emissive devices, each was doped at a concentration of 0.5% (by weight) with the pyromethene laser dye PM580 supplied by Exciton (Fig. 2).

Light-emitting diode devices based on doped single organic layers were fabricated on 24 mm square pieces of 10 Ω ITO coated glass (Balzers). Prior to use, the ITO was washed and UV–ozone treated. Polymer layers were deposited by spin coating from 1,2-dichlorobenzene, followed by a 10 minute hotplate bake at 75 °C to remove the solvent. Polymer concentrations of 4–5%, with spin speeds of 2000 to 3000 rpm provided dry layer thicknesses in the range 75 nm–140 nm. Cathode metalisation comprising 1000 Å of Mg followed by 1000 Å of Ag as a protective layer was deposited by thermal evaporation at a pressure of 2×10^{-6} Torr. The cathode was patterned by use of a shadow mask which defined circular devices each of area 9.61 mm^2.

Devices were driven using a computer-controlled Keithley 236 Source-Measure unit, while the brightness and spectral

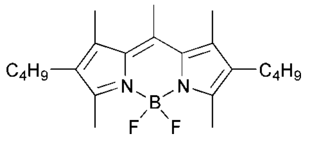


Fig. 2 Structure of luminescent dopant PM580.

properties of emitted light were measured using a Photoresearch imaging spectrophotometer type PR714, which recorded both the absolute luminance and the emission spectrum with a collection angle of 0.5°. The efficiencies of devices where quoted are derived from the brightness measured at normal incidence, taking account of the observed Lambertian emission from the devices.

In order to make reasonable comparisons between the copolymer and blend devices, the samples were prepared at the same time; thicknesses of the spun polymer layers were kept as similar as possible, and the cathode metals were deposited on both devices in the same chamber at the same time. Variations across the samples in emission intensity and in current–voltage (*I*–*V*) characteristics were observed to be very small, although all samples suffered degradation when operated at high current densities. All the spun polymer layers formed solid films with excellent physical properties. There was no sign of film reorganisation or crystallisation with time. Indeed the limiting factor affecting the lifetime of all the devices was oxidation of the reactive cathode material.

3 Results and discussion

3.1 Copolymer and polymer blend OLED devices

Fig. 3 shows the *I*–*V* characteristics for OLED devices made from either 124.9 nm layer of PVTPA : P3VPPO random copolymer or from a 111.6 nm thick film of a 1 : 1 blend of the homopolymers. There is a distinct difference between the two characteristics. Although both show a high turn-on voltage, the copolymer shows far greater current carrying capability, whilst current carried by the blend saturates at high voltages. The high operating voltage is attributed to a high potential for charge injection into the simple triphenylamine hole transport material. In Fig. 4, the variation in luminance as a function of current density is shown for the same two devices. The copolymer sample attains a respectable maximum brightness of 1200 cd m^{-2}, whilst the blend produces a maximum luminance of only 17 cd m^{-2}. All the devices reported showed an emission spectrum characteristic of the PM580 dopant; a representative spectrum is shown in Fig. 5. Using the gradients of the current–luminance graphs shown in Fig. 4 to establish the device quantum efficiency, the copolymer device achieves 0.148% whilst the blend quantum efficiency is 0.026%. A possible explanation for the differences in the efficiency, brightness and *I*–*V* characteristic is that the ratio of homopolymers, and hence carrier units, in the blend was different to that in the copolymer. The experiments were therefore repeated using a ratio of 1 : 1.9 PVTPA : P3VPPO in a polymer blend to duplicate the ratio in the copolymer. Once again, however, the resulting devices showed poor properties. Although the current carrying capacity and peak brightness (68 cd m^{-2} at 208 mA cm^{-2}) were raised compared to the 1 : 1 blend ratio, the efficiency was even lower. As the charge carriers in the polymer blend and copolymer devices are identical, the difference probably lies in the morphology of the layer and in particular in the occurrence of phase segregation in the blend.

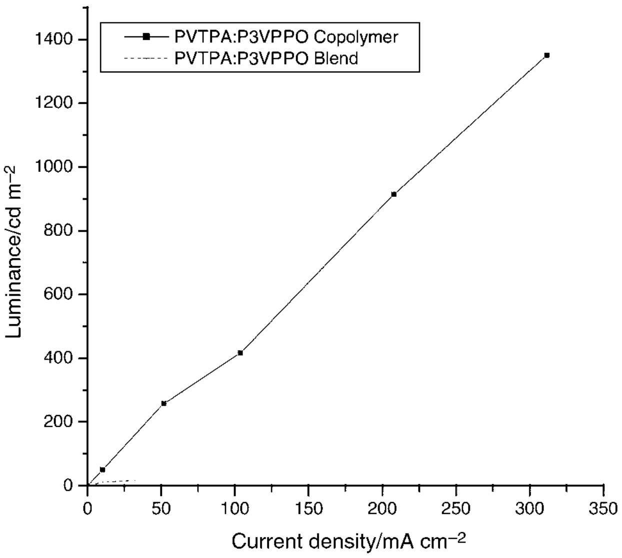


Fig. 4 Variation of luminance with current density for OLED devices made using PVTPA : P3VPPO copolymer (solid line) and blend (dashed line).

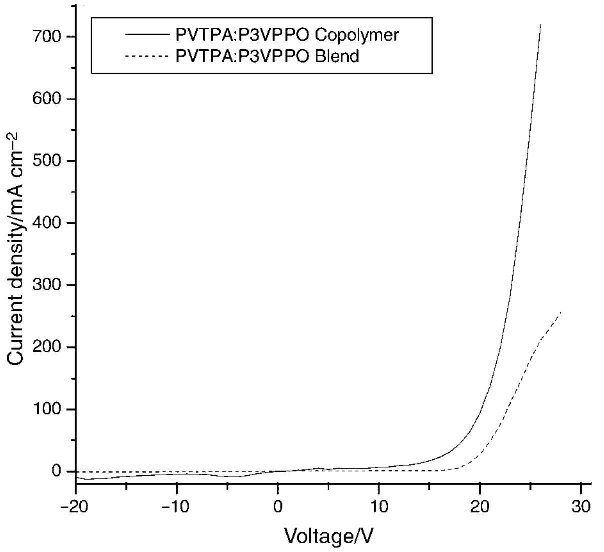


Fig. 3 Current density *versus* voltage characteristics for OLED devices made using PVTPA : P3VPPO copolymer (solid line) and blend (dashed line).

Similarly, OLED devices were made using a PVTPA : PVDPQ random copolymer and a 1 : 1 blend of the corresponding homopolymers. The organic layer thicknesses were 76 nm for the blend of homopolymers and 74.2 nm for the random copolymer. The *I*–*V* characteristics are shown in Fig. 6, and the variation of luminance with current density for each device is shown in Fig. 7. Both graphs show strong

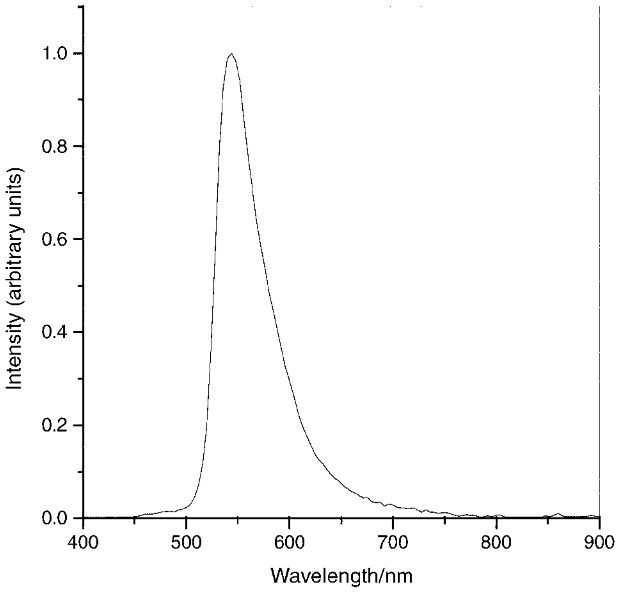


Fig. 5 Emission spectrum of a representative sidechain polymer device: PVTPA : P3VPPO copolymer + 0.5% PM580.

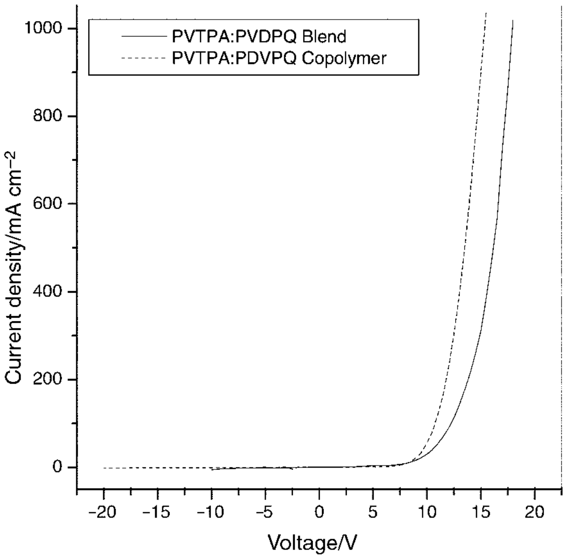


Fig. 6 Current density *versus* voltage characteristics for OLED devices made using PVTPA : PVDPQ copolymer (solid line) and blend (dashed line).

similarities between the two devices. The turn-on voltages of the devices based on quinoxaline polymers are approximately one half those of the oxadiazole polymer based OLEDS. This, however, is largely a reflection of the difference in organic layer thickness in the two types of device; the turn-on field for the quinoxaline based devices is a little lower than for the oxadiazoles, suggesting a barrier to charge injection for the diphenylquinoxaline group which is a little lower than for diphenyloxadiazole.

Under forward bias, both devices produce emission from the PM580 dopant peaking at 560 nm. Both devices demonstrate relatively high brightness for a single layer OLED, the maximum luminance of the blend being 2290 cd m^{-2} whilst the random copolymer achieves 1557 cd m^{-2} at the same current. Averaging over the whole luminance–current curve gives quantum efficiencies of 0.114 and 0.073% for the blend and copolymer respectively. The qualitative similarity of these results suggests correspondingly small structural differences between the copolymer film and the blend when VDPQ is used as the electron transport side chain. Similar results were obtained when devices were prepared from a mixture of PVTPA and PVDPQ, each having $M_n > 100\,000$. We infer from this that PVTPA and PVDPQ may be compatible polymers and consequently do not show phase separation. This hypothesis is supported by the observed yellow colouration of the copolymer, also seen in the blend of the two corresponding homopolymers, albeit much paler. Interaction between the two charge carrying moieties will encourage miscibility, indeed donor–acceptor interactions between pendant groups have been used in the design of miscible polymer systems.

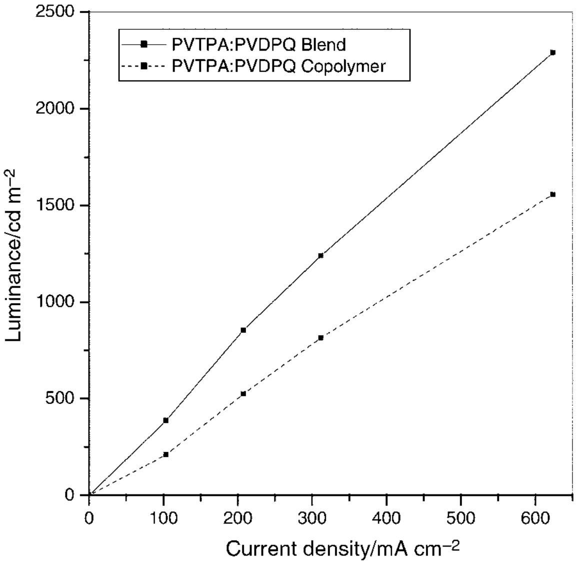


Fig. 7 Variation of luminance with current density for OLED devices made using the PVTPA : PVDPQ copolymer (solid line) and for the blend (dashed line).

We attempted to verify the phase behaviour of the polymer blends directly, both by DSC and by imaging of the spun layers by AFM in relief and phase contrast mode. No splitting of the glass transition processes could be seen in either mixture, while this provides some support for an absence of phase separation in the PVTPA–PVDPQ blend, it is not strong evidence since T_g values for PVTPA and P3VPPO are very similar. The AFM study was consistent with the miscibility hypothesis since either no phase segregation occurred or any phase separation which did occur did not provide observable contrast either in topography or in the mechanical properties of the layer.

An alternative route by which a PVTPA–PVDPQ polymer blend OLED device might provide a relatively high efficiency despite the occurrence of phase separation, is for each of the polymers to admit the injection and transport of a significant minority current. This possibility, together with the value of the materials as minority carrier blocking layers, was assessed by fabrication of homopolymer based devices.

3.2 Homopolymer test devices

Having obtained encouraging results and high luminance from single-layer devices incorporating side-chain units of both 3VPPO and VDPQ, devices were made using the homopolymers substituted with these same electron transport groups, in order to assess the minority charge carrier capacity of the materials. Once again films were doped with 0.5% PM580 which was present at too low a level to interfere with conduction, but which served as an indicator that recombination was taking place within the film. 'Hole-only' devices were made from spun films of P3VPPO and PVDPQ using ITO as an anode and gold, which is unfavourable for electron injection, as a cathode. The film thicknesses were 146 and 102 nm respectively. Fig. 8 shows the variation of current density with applied field for the two devices. The threshold for conduction lies at a considerably higher field for the quinoxaline

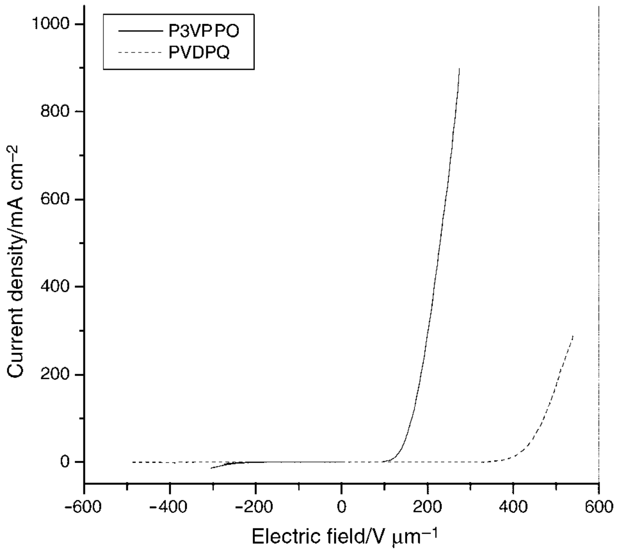


Fig. 8 *I–V* characteristics of hole only devices made using P3VPPO (solid line) and PVDPQ (dashed line) homopolymers.

homopolymer than for the oxadiazole, for both forward and reverse bias. The difference between the forward and reverse bias cases is explained by the relative work-functions of the gold and the ITO. Forward bias corresponds to hole injection from the ITO electrode. We note that the current passed under high bias fields in these devices could in principle be either hole or electron dominated. Electron injection from these electrodes, however, is expected to be unfavourable and should occur more readily from gold than ITO, which contradicts the observed asymmetry of the device characteristic. The results presented above on mixed carrier devices also indicate that electron injection into the diphenylquinoxaline layers is easier than into diphenyloxadiazole, contrary to the order of threshold field in these devices, so the current can with confidence be attributed to hole motion. Some emission of light was seen for both devices under forward bias, suggesting that at high fields, electron injection is also occurring at the gold electrode. From the turn-on voltages, clearly PVDPQ has hole blocking properties that are much superior to those of P3VPPO. This was confirmed further when dye doped homopolymer layers of the same thicknesses as those described above, on ITO glass substrates were coated with a Mg–Ag cathode. Under forward bias the P3VPPO produced a maximum EL emission intensity of 229 cd m^{-2} whilst the PVDPQ film EL emission reached only 6 cd m^{-2}, implying a much higher hole current in the oxadiazole polymer than in the quinoxaline derivative. It appears from these experiments that the quinoxaline based polymer provides an effective hole blocking layer, and minority carrier transport cannot explain the differences between copolymer and polymer blend devices. Hole blocking properties are necessary for the successful use of heterojunction device structures to confine carriers in a recombination zone and increase OLED efficiency. They are also important because injection of minority carriers has been proposed[22] as a source of instability in OLED devices which limits their operating life-times.

4 Conclusions

In this work we have studied two side-chain polymer electron-transport materials P3VPPO and PVDPQ. Single layer devices fabricated from random copolymers of the electron transport moieties under investigation and a hole-transport moiety PVTPA both give good performance. However when the devices are made from a blend of homopolymers very poor device performance is seen for P3VPPO whilst excellent performance is still obtained for PVDPQ. Phase separation of the two homopolymers is the likely explanation for the poor device performance of the P3VPPO : PVTPA blend although neither Atomic Force Microscopy nor DSC provide unequivocal evidence of this, perhaps due to the similar glass transition temperatures of the homopolymers. Perhaps surprisingly, the PVDPQ : PVTPA blend gives device performance which is comparable with the copolymer analogue; this suggests that the polymers are compatible and no phase separation occurs.

The results presented here allow a provisional judgement to be made of the relative merits of simple diphenylquinoxaline and diphenyloxadiazole groups as electron transport materials in OLED and other organic semiconductor devices. The brightness and operating efficiency of OLED devices incorporating each type of group are comparable (except for the PVTPA : P3VPPO blend). Although the peak brightness and efficiency of the quinoxaline devices are a little higher than those of the oxadiazoles, this may not be due to differences in the intrinsic properties of the charge carrying species, but may be a consequence of factors such as better balance of charge injection and lower operating voltage in the thinner devices. However, it appears that the properties of the quinoxaline group in respect of charge injection and electron transport are competitive and possibly superior to those of the oxadiazole. Of equal interest are the minority carrier properties of the materials. In this respect the quinoxaline material appears markedly superior. Initial results obtained in our laboratory on heterojunction devices lend support to this conclusion.

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References

1 J. L. Segura, *Acta Polym*, 1998, **49**, 319.
2 J. Kalinowski, *J. Phy.s D: Appl. Phys.*, 1999, **32**, R179.
3 R. C. Penwell, B. N. Ganguly and T. W. Smith, *Macromol. Rev.*, 1978, **13**, 63.
4 Y. Heischel and H. Schmidt, *Macromol. Chem. Phys.*, 1998, **199**, 869.
5 T. J. Boyd, Y. Geerts, J.-K. Lee, D. E. Fogg, G. G. Lavoie, R. R. Schrock and M. F. Rubner, *Macromolecules*, 1997, **30**, 3553.
6 J. Bisberg, W. J. Cumming, R. A. Gaudiana, K. D. Hutchinson, R. T. Ingwall, E. S. Kolb, P. G. Mehta, R. A. Minns and C. P. Petersen, *Macromolecules*, 1995, **28**, 386.
7 E. S. Kolb, R. A. Gaudiana and P. G. Mehta, *Macromolecules*, 1996, **29**, 2359.
8 F. Cacialli, X.-C. Li, R. H. Friend, S. C. Moratti and A. B. Holmes, *Synth. Met.*, 1995, **75**, 161.
9 W. J. Feast, R. J. Peace, I. C. Sage and E. L. Wood, *Polym. Bull.*, 1999, **42**, 167.
10 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **56**(9), 799.
11 B. Schulz, M. Bruma and L. Brehmer, *Adv. Mater*, .1997, **9**(8), 601.
12 X.-C. Li, A. B. Holmes, A. Kraft, S. C. Moratti, G. C. W. Spencer, F. Cacialli, J. Grüner and R. H. Friend, *J. Chem. Soc., Chem. Commun.*, 1995, 2211.
13 M. Strukelj, F. Papadimitrakopoulos, T. M. Miller and L. J. Rothberg, *Science*, 1995, **267**, 1969.
14 X.-C. Li, F. Cacialli, M. Giles, J. Gruner, R. H. Friend, A. B. Holmes, S. C. Moratti and T. M. Yong, *Adv. Mater.*, 1995, **7**(11), 898.
15 M. S. Weaver, D. G. Lidzey, T. A. Fisher, M. A. Pate, D. O'Brien, A. Bleyer, A. Tajbakhsh, D. D. C. Bradley, M. S. Skolnick and G. Hill, *Thin Solid Films*, 1996, **273**, 39.
16 J. F. Wang, Y. Kawabe, S. E. Shaheen, M. M. Morrell, G. E. Jabbour, P. A. Lee, J. Anderson, N. R. Armstrong, B. Kippelen, E. A. Mash and N. Peyghambarian, *Adv. Mater.*, 1998, **10**(3), 230.
17 M. Redecker, D. D. C. Bradley, M. Jandke and P. Strohriegl, *Appl. Phys. Lett*, .1999, **75**(1), 109.
18 V. I. Grigor'eva and R. S. Mil'ner, *Chem. Heterocycl. Compd.*, 1968, **4**(1), 23.
19 I. S. Poddubnyi, L. I. Bolen'kii, M. I. Struchova and M. M. Krayushkin, *Chem. Heterocycl. Compd.*, 1994, **30**(6), 729.
20 D. Braun and G. Quarg, *Angew. Makromol. Chem.*, 1975, **43**, 125.
21 G. Manecke and U. Rotter, *Makromol. Chem.*, 1973, **171**, 49.
22 Z. D. Popovic, H. Aziz, N.-X. Hu, A.-M. Hor and G. Xu, *Synth. Met.*, 2000, **111–112**, 229.