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Influence of molecular structure on the properties of dendrimer light-emitting diodes

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Abstract

Iridium-based phosphorescent dendrimers have shown much promise as highly efficient light emitting materials for organic light emitting diodes (OLEDs). Here we report the effects of modifying the chemical structure on the emissive and charge transport properties of Ir(ppy)$_3$ based electrophosphorescent dendrimers. We investigate a novel *para* linked first generation (G1) iridium dendrimer. This material is compared to G1 and G2 *meta* linked dendrimers. We show that by blending these dendrimers into a CBP host, high external quantum efficiencies of over 10% and luminous efficiencies of 27 lm/W can be achieved.

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1. Introduction

Research into new materials has played an important part in the development of organic light-emitting diodes (OLEDs). There are currently three main classes of materials for OLEDs: small organic molecules [1], conjugated polymers [2] and conjugated dendrimers [3,4]. Small organic materials have precisely defined structures and are generally processed by evaporation. In contrast polymers and dendrimers are processed from solution.

Recent developments in materials have led to a breakthrough in device efficiency through triplet harvesting in organic LEDs [5]. The technique of using a heavy metal containing phosphor to extract radiative emission from triplet states [6] has been very successful for thermally evaporated small molecules. This has allowed unprecedented efficiencies to be realised with internal quantum efficiencies of nearly 100% obtained [7].

Solution-processing of organic materials is a useful alternative for OLED fabrication as it offers scope for printing the organic layer, and so is likely to lead to advantages in commercial production. It would therefore be desirable to have a solution processible electrophosphorescent material.

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Various studies have been done using polymers as host materials for phosphorescent molecules [8–13], although efficiencies are still significantly lower than those offered by evaporated devices. The choice of a host polymer with a suitable triplet level is crucial to the performance of these devices. Poly(fluorene) and several of its derivatives have been used successfully as hosts for red emitting phosphors [8–10], however it does not possess a high enough triplet level for green emitting phosphorescent complexes [14]. Poly-*N*-vinyl carbazole (PVK) is a material with a suitable triplet level and has shown high external quantum efficiency (EQEs) when doped with phosphorescent dyes [11,12]. However its use often leads to very high operating voltages and consequently low power efficiencies.

We have investigated conjugated dendrimers as an alternative class of light emitting materials for organic LEDs [4,15–20]. These molecules consist of a core, conjugated dendrons (branches) and surface groups. The core defines the key electronic properties such as the colour of light emission. The way the dendrons are attached to the core can modify its electronic properties. The generation number of a dendrimer is defined as the number of branching levels from the core, and this can be used to control intermolecular interactions of the cores on a nanometre scale. This has been shown to give control of the majority carrier mobility with generation in dendrimer LEDs [17,18]. The surface groups are at the distal ends of the dendritic macromolecule, and therefore primarily define the solubility and processing properties.

We have reported both single [19] and bilayer [20] devices based on phosphorescent dendrimers or phosphorescent dendrimer blend systems. Systematic alteration of the generation number and connectivity to the core have been shown to give a fine control of the hole mobility in neat films, with a concomitant effect on the efficiency of devices for both single layer and bilayer systems [21]. However the effect of these structural modifications when the dendrimer is dispersed in a wide gap host material has not yet been investigated. The aim of this paper is to elucidate the effect of dendrimer structure when doped into a 4,4′-bis(*N*-carbazolyl) biphenyl (CBP) host material.

2. Experiment

The dendrimers studied here are comprised of a *fac*-tris(2-phenylpyridine) iridium III (Ir(ppy)$_3$) core, phenylene dendrons and 2-ethylhexyloxy surface groups. They are: G1-*meta*-Ir(ppy)$_3$(G1*m*Ir), G1-*para*-Ir(ppy)$_3$ (G1*p*Ir) and G2-*meta*-(ppy)$_3$ (G2*m*Ir), and the structures are shown in Fig. 1.

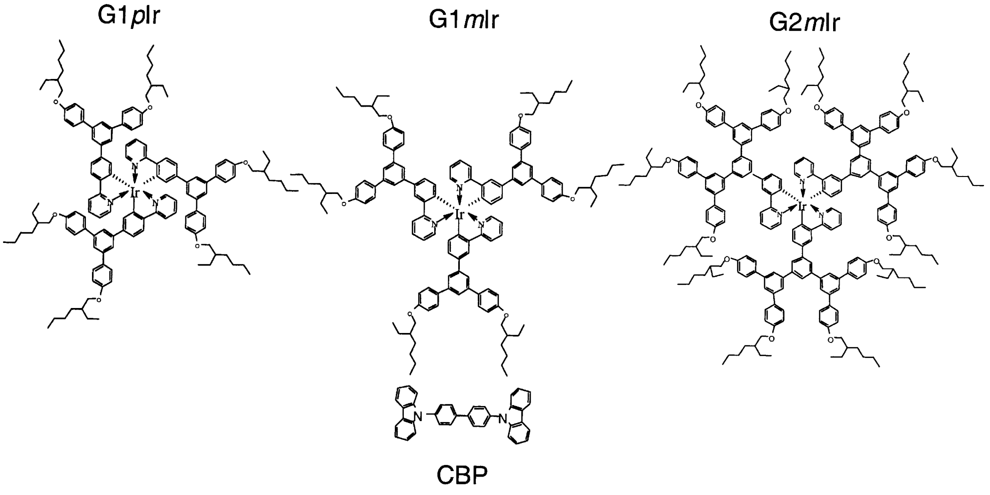

Fig. 1. Structures of G1*p*Ir, G1*m*Ir and G2*m*Ir iridium cored dendrimers. Also shown is the structure of CBP.

This family of closely related materials can offer us insight into the effect of generation and dendron attachment point on the optical, electronic and morphological properties of dendrimer and dendrimer doped films. The dendrimers are soluble in polar aprotic solvents such as tetrahydrofuran and chloroform. Dendrimer: CBP blend films were spin coated from 15 mg/ml chloroform solutions to give film thicknesses of approximately 80 nm.

The etched indium tin oxide (ITO) substrates were cleaned sequentially in ultrasonic baths of acetone and 2-propanol, before oxygen plasma ashing under a pressure of 10^{-2} mbar at 100 W for 5 min (Emitech Model K-1050X). Bilayer devices were fabricated by evaporation of 70 nm of 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) as an electron transporting/hole blocking layer and a cathode of 0.4 nm LiF and 15 nm of calcium capped with 100 nm aluminium completed the device. The pixel area was approximately 6 mm^2.

3. Results

The three dendrimers were doped into a CBP host to act as the emissive layer in bilayer OLEDs. CBP has been shown to be an effective host for single layer dendrimer blend LEDs [19] and is expected to show similar performance in bilayer devices. 6 wt% of Ir(ppy)_3 in CBP has been shown to be optimal for evaporated small molecular devices [22]. In our dendrimer LEDs we have therefore used the same molar concentration of iridium chromophores, as is present in 6 wt% of Ir(ppy)_3 in CBP. This concentration was found to be optimal for spin-coated single layer dendrimer devices [19] and has the additional feature that holes are carried efficiently by hopping between Ir(ppy)_3 sites [22]. G1*m*Ir and G1*p*Ir have identical molecular weights, so the appropriate molar concentration was achieved for 20 wt% of these materials in CBP. The equivalent molar concentration of G2*m*Ir required blends containing 36 wt% of the dendrimer in CBP. The larger dendrons of the G2*m*Ir material might be expected to lead to improved film forming properties.

The photoluminescence quantum yields (PLQYs) of these blends have been measured using an integrating sphere. Excitation of the samples was by the 325 nm line of a helium–cadmium laser. Very high PLQYs were measured for these films: 78% for G1*m*Ir:CBP, 68% for G1*p*Ir:CBP and 80% for G2*m*Ir:CBP. Bilayer devices were fabricated with the structure ITO/dendrimer:CBP/TPBI/LiF/Ca/Al. An evaporated layer of TPBI has been used previously for iridium dendrimer bilayer systems [20] and found to be an effective electron transport/hole blocking medium. A trilayer LiF/Ca/Al contact offers improved electron injection into the TPBI LUMO over LiF/Al or Ca/Al [23].

The EL spectra of the bilayer devices are shown in Fig. 2. It can be seen that for the *meta* linked materials the emission is the same for the first and second generation materials and is identical to the parent Ir(ppy)_3 core in a CBP host. This illustrates that addition of the biphenyl dendrons in the *meta*-position of the phenyl ring (relative to the pyridyl) attached to the metal does not alter the electronic properties of the core. Vibrant green emission is observed with a peak at 518 nm and CIE coordinates of ($x = 0.31$, $y = 0.63$). The emission of the dendrimer with the dendron in the *para* position relative to the pyridyl ring is redshifted by 17 nm to give yellow–green emission with a peak at 535 nm ($x = 0.42$, $y = 0.56$) due to the extended conjugation of the ligand chromophore attached to the iridium cation.

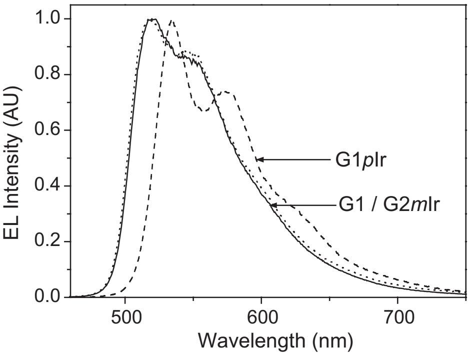

Fig. 2. The electroluminescence spectra of dendrimer blend bilayer devices. Shown are G1*m*Ir (solid line), G1*p*Ir (dashed line) and G2*m*Ir (dotted line).

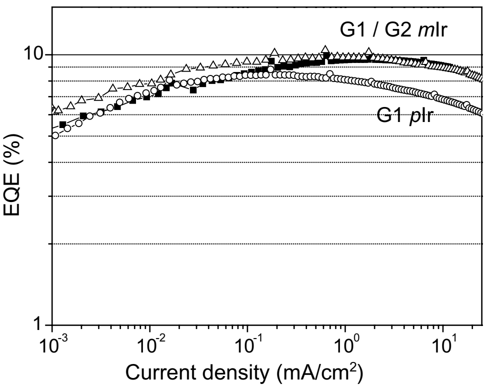

Fig. 3. Double log plot of external quantum efficiency as a function of current density for G1*m*Ir (squares), G1*p*Ir (circles) and G2*m*Ir (triangles).

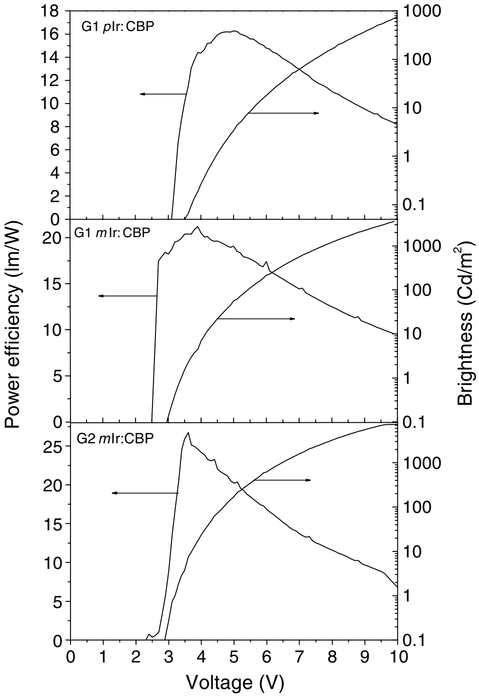

Fig. 4. Luminous efficiency and brightness for the three blends studied. From top: G1*p*Ir, G1*m*Ir and G2*m*Ir.

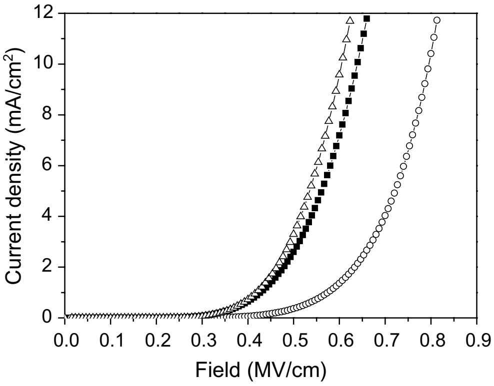

Fig. 5. Current density as a function of field for G1*m*Ir (squares), G1*p*Ir (circles) and G2*m*Ir (triangles) blend devices.

All the devices were very efficient and the external quantum efficiencies as a function of current density are shown in Fig. 3. Whereas the performance of devices based on neat films is heavily dependent upon dendrimer structure [19], the three materials dispersed in a charge transporting host show similar properties as a function of current density. The 20 wt% G1*p*Ir in CBP blend has a peak EQE of 8.8% (30.1 Cd/A) whilst the 20 wt% G1*m*Ir in CBP and 36 wt% G2*m*Ir in CBP blends show slightly improved performance with 9.8% (33 Cd/A) and 10.4% (34.3 Cd/A). These high efficiencies are maintained across a large range of current densities, illustrating a good level of confinement by the bilayer structure. This is in contrast to single layer devices utilising CBP as a host where the EQE is seen to rise as a function of current density [19]. This effect has been attributed to a saturation of non-radiative sites with increasing current density [22] and a deficiency in electron transport in the dendrimer:CBP blend at low currents. We attribute the slightly lower efficiency of the G1*p*Ir:CBP blend, at least in part, to the lower PLQY of this system.

The luminous efficiencies and light outputs of the three blend systems are shown in Fig. 4. The best luminous efficiencies were observed for G2*m*Ir:CBP devices, possibly due to the better film forming properties of this blend. A peak luminous efficiency of 27 lm/W (at 8 Cd/m^2), 22 lm/W (at 100 Cd/m^2) and 15.5 lm/W (at 1000 Cd/m^2) were measured. G1*m*Ir:CBP had a slightly lower luminous efficiency of 21 lm/W and G1*p* Ir:CBP lower still at 16.3 lm/W. An interesting characteristic is the increase in operating field (Fig. 5) for a given current density with the sequence G2*m*Ir, G1*m*Ir, G1*p*Ir. This is in direct contrast to the zero field mobilities measured for neat films of these materials [21], and the performance of neat single layer devices [19]. A possible explanation could be better film formation in the G2 blend. This could lead to a more homogeneous distribution of emitting sites within the film. As there is approximately a 300 meV difference in the HOMO energy levels of the dendrimers and CBP, hopping most likely occurs between dendrimer sites. Hopping mobilities in dendrimers have been shown to have an exponential dependence on site separation [17,18], and thus increased levels of aggregation will increase the hopping distance, and lead to a more insulating film. This may be a possible explanation for the observed *I–V* curves of the *para* linked material.

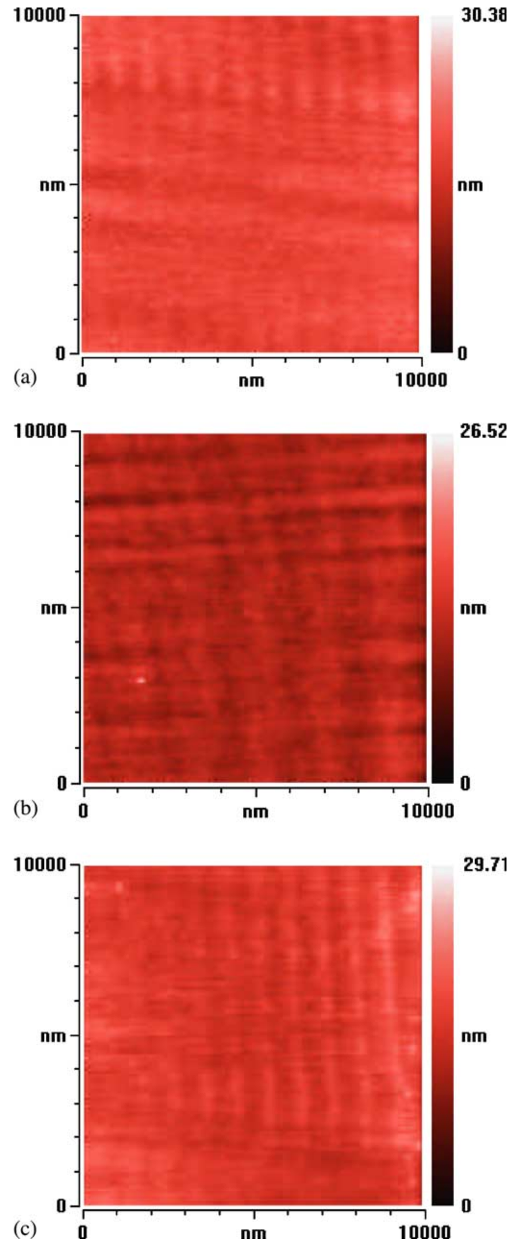

Fig. 6. AFM images of (a) G1*m*Ir:CBP, (b) G1*p*Ir:CBP and (c) G2*m*Ir:CBP films.

We have examined the blend films by atomic force microscopy (AFM). Some polymer blend systems phase separate and AFM has been shown to be a powerful tool in the analysis of this behaviour [14]. AFM images of ~80 nm thick films of the three blends spun onto plasma treated ITO are shown in Fig. 6. The surface profile indicates that films are smooth and the root mean square (RMS) surface roughness is ~2.5 nm. The film quality of our CBP doped dendrimer blends are similar to the recently reported spin coated poly(*n*-vinylcarbazol) doped Ir(ppy)$_3$ (8% by weight) film [14]. Hence we cannot detect any phase separation in our dendrimer:CBP blends, in contrast to some polymer blend systems.

In conclusion, we have shown that the optical and electronic properties of iridium-cored dendrimers can be modified by the location and size of the dendritic group. Irrespective of the generation or configuration of the dendrimer, we are able to achieve excellent miscibility with a CBP host, form good films, and make very efficient devices.

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