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Multi-layer organic light-emitting diodes processed from solution using phosphorescent dendrimers in a polymer host

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ABSTRACT

A uniform dispersion of highly soluble phosphorescent dendrimer emitters is achieved by blending with a polymer host poly(9-vinylcarbazole) (PVK) containing *N,N′*-diphenyl-*N,N′*-(bis(3-methylphenyl)-[1,1-biphenyl]-4,4′-diamine (TPD) and 2-(4-biphen-4′-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD). No visible aggregation or self-quenching was observed for guest-to-host weight ratios of up to 33:67. The dendrimers contain a *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$] core, first generation biphenyl-based dendrons, and 2-ethylhexyloxy surface groups. The guest–host blend is used for all solution processed organic light-emitting diodes. A maximum external and current efficiency of 10.2% and 38 cd/A (at 5 V and a brightness of 50 cd/m^2), and a maximum brightness of 27,000 cd/m^2 (at 14.5 V), were obtained when a CsF/Al cathode was used. Blade coating was used to fabricate a multi-layer structure that also contained an electron-transport layer. The device that had a LiF/Al cathode had a maximal efficiency of 40 cd/A corresponding to an external quantum efficiency of 10.8% (at 5 V and a brightness of 19 cd/m^2). The maximum brightness of the second device was 17,840 cd/m^2 at 14 V.

1. Introduction

Solution processable organic light-emitting diodes (OLEDs) have the great potential for applications in large-area lighting and displays [1]. Compared with fluorescent OLEDs, phosphorescent OLEDs have much higher efficiency because the triplet emitters used can theoretically harvest 100% of the excitons that are formed during device operation [2]. A common way to achieve efficient phosphorescent OLEDs is to blend heavy metal complexes such as iridium(III) or platinum(II) complexes into polymer hosts. However, a major challenge for such simple blending is that small molecule phosphorescent emitters in general have poor solubility, resulting in aggregation in the polymer host. In fact most of the iridium(III) complexes are vacuum deposited where aggregation is avoided by careful co-evaporation together with a small molecule host [3,4]. Aggregation of the iridium(III) complexes in the polymer hosts reduces the electroluminescence efficiency due to two reasons. One is the quenching of the luminescence through triplet–triplet annihilation, and the second is that aggregation may leave some volume in the host without any emitter so the exciton will form and decay in the host. The hosts often have a low radiative decay efficiency and emit light of a different color to the guest complex. In order to raise the efficiency of solution processed polymer based light-emitting diodes to the level of vacuum deposited small molecule organic light-emitting diode, the dispersion

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of the metal complex emitter in the polymer host must be improved.

Chemical modification of the phosphorescent green iridium(III) complex *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$], which has been shown to have a high photoluminescence efficiency and relatively short radiative lifetime, has led to some improvement in the solubility. For example, methylation of Ir(ppy)$_3$ on the ligand phenyl ring at the position *para* to the ligand pyridyl ring, i.e. tris[2-(4-tolyl)pyridyl]iridium(III), [Ir(mppy)$_3$], enhances the solubility. However, although the solubility is improved, this approach still does not fully prevent the aggregation of the emissive molecules. This is due to Ir(mppy)$_3$ still having only poor to at best moderate solubility in organic solvents commonly used for processing polymer hosts such as toluene and chlorobenzene. The range of concentrations that the complex is used as a guest in a polymer host in which a uniform dispersion is achieved is therefore quite limited. Moreover, the low solubility of Ir(mppy)$_3$ makes it difficult to accurately control the doping concentrations and the long mixing time required for dissolution makes the fabrication process rather time-inefficient.

Dendrimer OLEDs offer the advantages of combining the high efficiency of small molecule OLEDs and the solution processing properties of polymer OLEDs [5,6]. High efficiency dendrimer OLEDs have been achieved when the dendrimer layer has been deposited by spin-coating, and an evaporated electron-transport layer has been used [7–9]. Lately, blade coating has shown potential as an alternative processing method to spin-coating and ink-jet printing. It also opens up the possibility of multi-layer OLEDs, in which all the layers are deposited by solution processing [10] without the use of post UV-cured polymerization of soluble cross-linkable precursors [11]. In general multi-layer structures are required to balance electron and hole currents for achieving highly efficient OLEDs.

In this Letter we use highly soluble dendrimers, p-G1-Ir and m-G1-Ir, as the light-emitting guest (chemical structures shown in Fig. 1c). The host is a mixture comprised of poly(9-vinylcarbazole) (PVK), and charge-transport materials, *N,N′-diphenyl-N,N′*-[bis(3-methylphenyl)]-[1,1′-biphenyl]-4,4′-diamine (TPD) and 2-(4-biphen-4′-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [12]. The p-G1-Ir and m-G1-Ir dendrimers consist of a *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$] core, first generation biphenyl-based dendrons, and 2-ethylhexyloxy surface groups [13,14]. The synthesis of the dendrimers has been previously reported [15]. As shown in Fig. 1c, the difference between p-G1-Ir and m-G1-Ir is that p-G1-Ir has the dendron attached on the ligand phenyl ring *para* to the pyridyl ring whereas m-G1-Ir has the dendron attached on the ligand phenyl ring *meta* to the pyridyl ring [7,15,16]. Unlike most phosphorescent emitters based on small molecules, the phosphorescent dendrimers have superb solubility in common organic solvents due to the surface groups attached to the distal ends of the dendrons. In addition, the dendrons act as rigid spacers that reduce the intermolecular interactions of the emissive cores that can cause luminescence quenching [5,6,17]. Indeed, there is dramatic difference in solubility between the dendrimers used and Ir(mppy)$_3$. The solubility of p-G1-Ir is more than

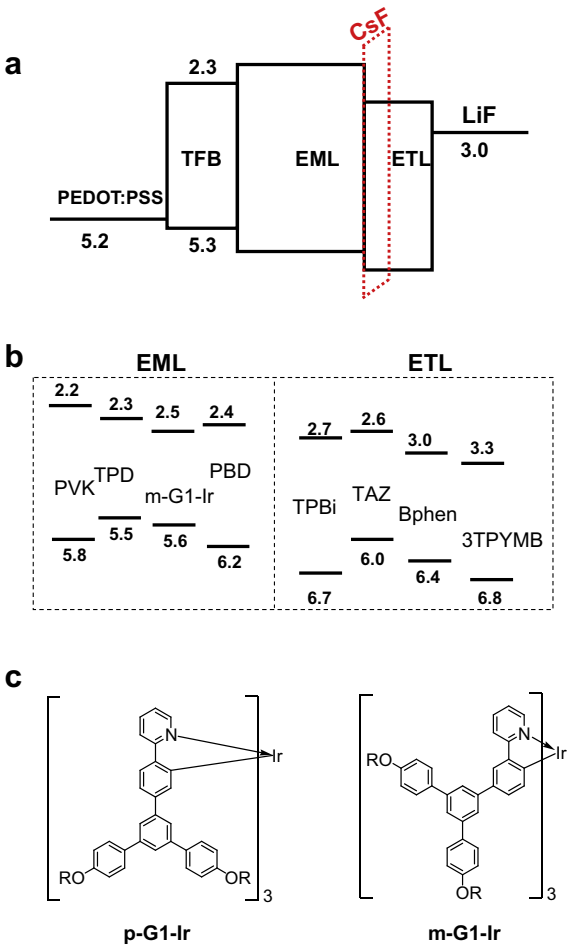

Fig. 1. (a) Schematic diagram of the OLED structures employed. The cathodes are CsF/Al for the devices without the ETL and LiF/Al for those with the ETL. (b) Energy diagram of the materials in this work, the numbers are in eV. (c) Structures of p-G1-Ir and m-G1-Ir.

10 wt.% both in toluene and chlorobenzene, whereas Ir(mppy)$_3$ is less than 0.5 wt.% in chlorobenzene and it is virtually insoluble in toluene. Bi-layer OLEDs with CsF/Al cathode and tri-layer OLEDs with an electron-transport layer (ETL) and a more stable LiF/Al cathode were fabricated with the dendrimers as the guest in a PVK:TPD:PBD blend host. The electron transport materials were deposited by a newly developed blade-coating method to avoid dissolution [10]. The ETL materials studied included 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi), 3-(4-biphen-4′-yl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ), 4,7-diphenyl-1,10-phenanthroline (Bphen), and tris-[3-(3-pyridyl)mesityl]borane (3TPYMB). High efficiencies were achieved for dendrimer weight concentrations of up to 33% with easy concentration control and instant dissolution during fabrication. An efficiency of 38 cd/A (at 5 V) and luminance of 27,000 cd/m^2 (at 14.5 V) were obtained in the bi-layer devices prepared by blade coating. Although direct comparison is not possible as different host materials have different solubility for the studies, current device efficiencies are higher than

those previously reported for similar bi-layer device fabricated from spin-coating [18]. In addition, the amount of dendrimer used in the emissive layer is less than that of previous reports, making the blade-coating fabrication more cost effective.

2. Experimental

Fig. 1 shows the OLED device structures used in the study. To fabricate the OLEDs, the indium-tin-oxide (ITO) substrate was first precleaned in deionized water with detergent, which was purchased from Alconox, and then UV–ozone treated. In order to use the blade-coating technique it was necessary to have large ITO substrates (7 cm × 8 cm). A 50 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP AI 4083) was then spin-coated onto the ITO substrate and annealed at 100 °C for 40 min in vacuum. To improve hole injection in the devices [19,20], poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(4,4′-{*N*-[4-*s*-butylphenyl]}diphenylamine)] (TFB) in toluene (1 wt.%) was blade-coated on top of the PEDOT:PSS and spin-rinsed with toluene after annealing at 180 °C for 40 min in vacuum to leave a TFB layer with thickness of about 5 nm. The light-emitting solution was prepared by mixing host solution, PVK:PBD:TPD in chlorobenzene (2 wt.%), and dendrimer guest solution, dendrimer in toluene (2 wt.%), and then blade-coated onto the TFB layer to give a 70 nm thick 'light-emitting' film. In the blend system, dendrimer:PVK:TPD:PBD, the ratio of TPD:PBD was fixed at 9:24 and the ratio of dendrimer:PVK was tuned. The ratios of p-G1-Ir:PVK were 1:66, 2:65, 6:61, 13:54, and 33:34. The ratios of m-G1-Ir:PVK were 2:65, 6:61, 13:54, and 33:34. The emissive layer was annealed at 80 °C for 60 min in vacuum. To complete the devices without an electron-transport layer, a 2 nm layer of CsF was deposited, followed by a 100 nm capping layer of Al. The latter two layers were deposited using thermal evaporation at a pressure of 10^{-6} Torr. For the devices with electron-transport layers, TPBi, TAZ, Bphen, and 3TPYMB, were dissolved in *n*-butanol (0.5 wt.%) and blade-coated on top of the emissive layer (dendrimer:TPD:PBD:PVK with a ratio of 6:9:24:61) to give thicknesses of order 20 nm [12]. Dissolution between the ETL and emissive layer was avoided by using the newly developed blade-coating method with *n*-butanol as the solvent. A thin (≈1 nm) layer of LiF was evaporated under the pressure of 10^{-6} Torr and covered with a 100 nm of Al to form the cathode and complete the devices. The active area of each pixel was 4 mm^2. *I–L–V* characteristics were measured with a Keithley 2400 source meter with the light output integrated with a PR650 photometer. PVK with a molecular weight (M_w) of 1,100,000 was purchased from Sigma–Aldrich. TPD, PBD, TPBi, TAZ, BPhen, and 3TPYMB were obtained from Luminescence Technology Corp, and TFB was purchased from American Dye Source.

3. Results and discussion

Figs. 2 and 3 show the bi-layer device characteristics and emission spectra based on p-G1-Ir and m-G1-Ir, respectively, and using CsF/Al as cathode. In general, the

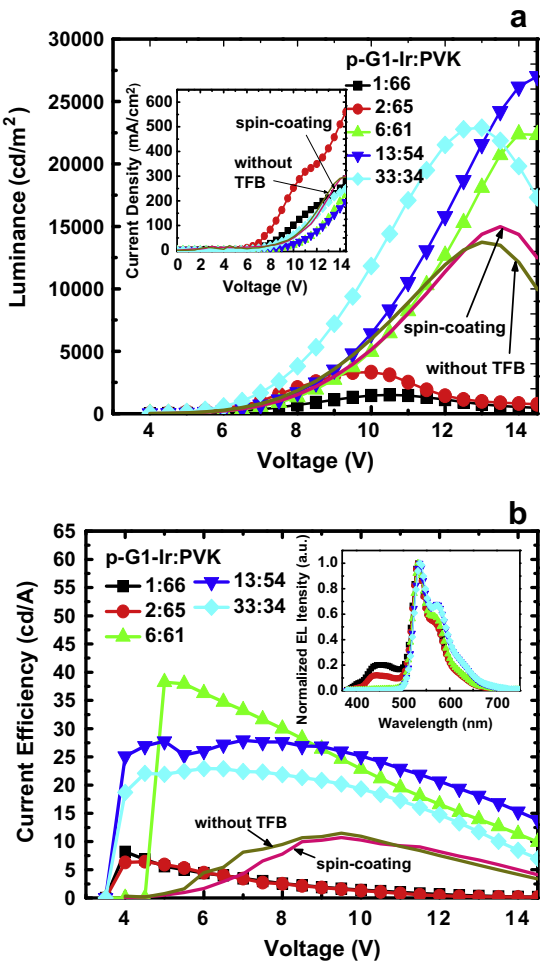

Fig. 2. Device performance of p-G1-Ir:PVK:TPD:PBD. (a) The luminance and the inset is the current density *versus* voltage. (b) The current efficiency *versus* voltage and the inset shows the electroluminescent spectra at 1000 cd/m^2. The ratio of TPD:PBD was fixed at 9:24. The performance of the device without TFB layer is indicated by dark yellow line, while the performance of the device fabricated by spin-coating instead of blade coating is indicated by pink line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

luminance and efficiency were not high at low dendrimer doping concentrations in the PVK (i.e. 1:66 and 2:65 with a fixed ratio of TPD:PBD of 9:24). This could be due to the fact that there were not enough emitters in the host to harvest the excitons, which is supported by the emission spectra where there is blue emission from the host (Fig. 2b). The blue emission at the wavelengths near 400 nm can be attributed to the TPD or PVK host while the broad emission peaking at 470 nm may originate from the $(TPD + PBD-)^*$ exciplex [12]. Interestingly, the blue emission from m-G1-Ir based devices is not as obvious as those of p-G1-Ir at the same doping concentration (2:65) (Fig. 3). Given that the two dendrimers have exact the same molecular weights and the same dendrimer doping concentrations, the smaller amount of blue emission from the (2:65) device could be due to the different shape of the dendrimers. The different shape results from the dendrons

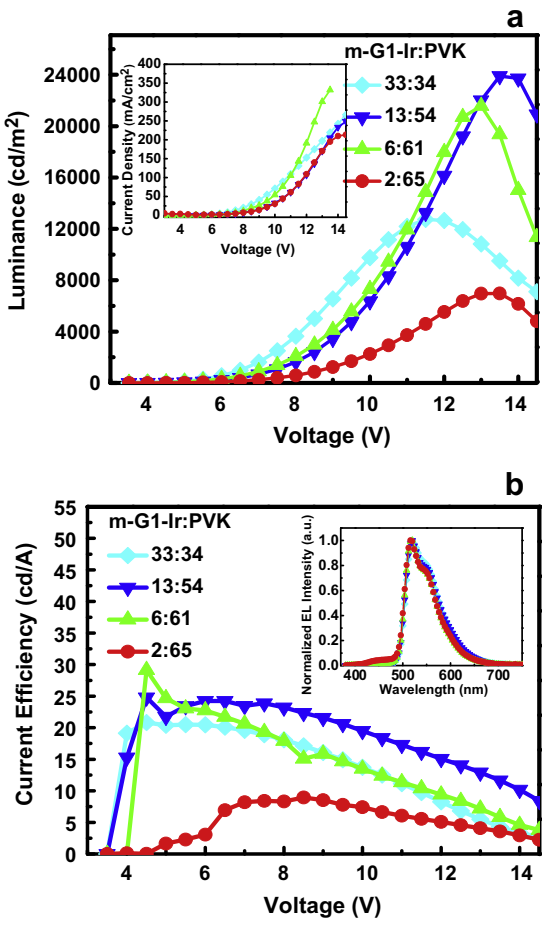

Fig. 3. Device performance of the m-G1-Ir:PVK:TPD:PBD. (a) The luminance and the inset shows the current density *versus* voltage. (b) The current efficiency *versus* voltage and the inset is the electroluminescent spectra at 1000 cd/m^2. The ratio of TPD:PBD was fixed at 9:24.

being attached to different positions on the ligand phenyl ring of the emissive core, which in turn could give rise to a different film morphology. The fact that m-G1-Ir has a larger effective hydrodynamic radii is evidence of the difference in shape between the two materials [15].

Both the luminance and efficiency significantly increased as the dendrimer concentrations increased above the ratio of 6:9:24:61 [dendrimer:TPD:PBD:PVK (TPD:PBD:PVK = host)]. The peak luminance of 22,900 cd/m^2 (at 13 V), 27,000 cd/m^2 (at 14.5 V), and 22,380 cd/m^2 (at 14 V) was achieved for p-G1-Ir:PVK with blending ratios of 33:34, 13:54, and 6:61, respectively. The current efficiency was around 22–38 cd/A for the mixing ratios of dendrimer:PVK between 33:34 and 6:61, showing that the dendrimers can be used in rather high blending concentrations due to the uniform distribution in the emissive layer with less aggregation and self-quenching. The highest external quantum efficiency is 10.2% at 5 V with a brightness of 50.1 cd/m^2 for p-G1-Ir:PVK at ratio of 6:61. Such excellent dispersion in the polymer host is attributed to the good solubility of the dendrimers in comparison to small molecule iridium(III) complexes.

While the efficiency of device with a p-G1-Ir:PVK ratio of 6:61 reaches up to 40 cd/A, it drops rapidly as the voltage increases. In contrast, the devices with a p-G1-Ir:PVK ratio of 13:54 keeps a high efficiency at high luminance. In fact the ratio 13:54 of dendrimer:PVK was found to be the optimum ratio for both dendrimers in the host. For OLEDs with higher dendrimer concentrations, although the dispersion is still good, some level of self-quenching sets in causing a slight reduction in the efficiency.

The significance of the blade-coating method can be understood from the performance of the device fabricated by spin-coating. The concentration ratio of p-G1-Ir:PVK is 6:61. As shown in Fig. 2, the luminance and current efficiency are low for the device fabricated by spin-coating. The peak luminance of 14,980 cd/m^2 was achieved at 13.5 V, and the maximum current efficiency of 10.7 cd/A was achieved at 9.5 V. This inferior performance may result from the layer-to-layer dissolution while using spin-coating technique or due to a completely different film morphology being formed. The layer-to-layer dissolution can be prevent by adopting the blade-coating technique as described in previous work [10]. The need for the TFB layer is

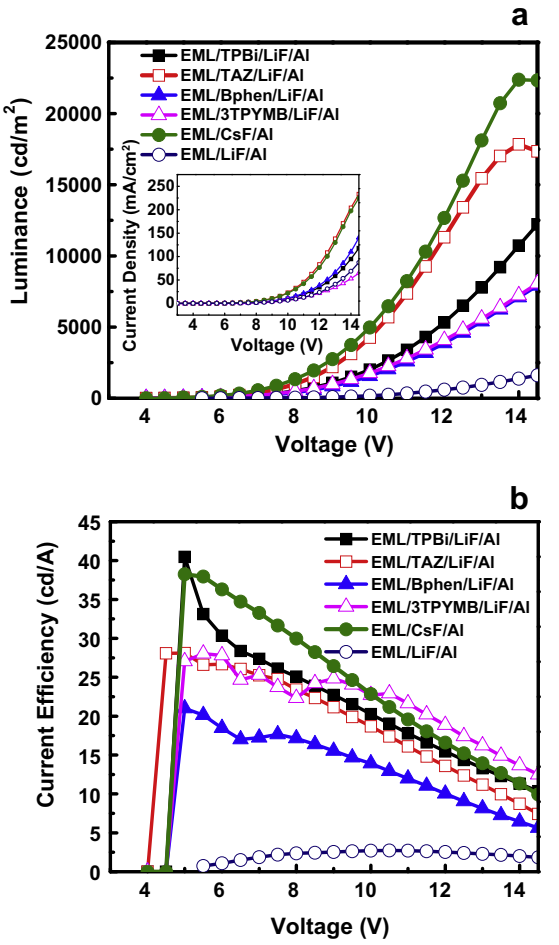

Fig. 4. The results of the multi-layer p-G1-Ir:PVK:TPD:PBD devices with ETL materials, TPBi, TAZ, Bphen, and 3TPYMB. (a) The luminance and the inset is the current density *versus* voltage. (b) The current efficiency *versus* voltage.

also shown in Fig. 2. For the device without TFB hole-transporting and electron-blocking layer, the peak luminance of 13,730 cd/m^2 was achieved at 13 V, and the maximum current efficiency of 11.5 cd/A was achieved at 9.5 V. The superior performance of the device with TFB layer results from the fact that more holes can be injected.

Fig. 4 shows the performance of the devices with TPBi, TAZ, Bphen, and 3TPYMB as the electron-transport layers and p-G1-Ir as the emitter. The ratio of dendrimer:TPD:PBD:PVK was 6:9:24:61. The results were compared with those without the electron-transport layer. Of the tri-layer devices, the device with TAZ shows the highest luminance as it and PBD have highest electron affinities [most stable Lowest Unoccupied Molecular Orbital (LUMO) energies] and this leads to more efficient electron injection into the light-emitting layer. However, the overall efficiency of TAZ devices is slightly lower than those containing TPBi. The device that had a LiF/Al cathode had a maximal efficiency of 40 cd/A (at 5 V with external quantum efficiency = 10.8% and brightness of 19 cd/m^2) and maximal luminance of 17,840 cd/m^2 (at 14 V). This difference probably arises from the fact that while the TAZ has the higher electron affinity it is a poorer hole blocking material than TPBi (see energy diagram Fig. 1b). In general the electron-transport layer in combination with LiF/Al cathode shows similar performance to devices with CsF/Al cathode but the latter devices tend to be less stable to the moisture. Without the electron-transport layer, the LiF/Al cathode has poorer electron injection capability and this may be due to a poor metal/organic interface leading to relatively low efficiencies (Fig. 4). The blade-coated layer of the electron transport materials therefore has a similar effect as with the equivalent vacuum deposited layers. Importantly, there is no dissolution of the emissive layer observed while blade coating the electron-transport layer.

4. Conclusion

In conclusion, we demonstrate that the good solubility of phosphorescent dendrimer emitters allows the formation of a dispersion of the dendrimers in a polymer host. The uniform dispersion enabled OLEDs with high efficiency and luminance to be achieved with a wide range of emitter concentrations because of low level of intermolecular quenching of the phosphorescence. The good compatibility of the phosphorescent dendrimers and the polymer host indicates that it is crucial to add functional groups to enhance the solubility when designing solution processable triplet emitters for use in blends. Importantly, all solution processed multi-layer OLEDs without layer-to-layer dissolution can be fabricated using the blade-coating technique. Blade-coating phosphorescent dendrimers show promise for the development of large-area and low-cost lighting emitting applications.

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