

The 'double dendron' approach to host free phosphorescent poly(dendrimer) OLEDs

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Received 3rd November 2011, Accepted 19th December 2011

DOI: 10.1039/c2py00519k

The addition of dendrons to iridium(III) complexes attached to a poly(styrene) backbone is shown to improve the physical and optoelectronic properties of the phosphorescent materials. The iridium(III) complexes have two 2-phenylpyridyl ligands and one phenyltriazolyl ligand, with the latter providing the attachment point to the polymer backbone. It was found that by increasing the number of dendrons (from zero to two) per 2-phenylpyridyl ligand, the intra- and interchain interactions could be more effectively controlled. The poly(dendrimer) with two dendrons per ligand had solution and solid-state photoluminescence quantum yields of 67% and 47%, respectively. Organic light-emitting diodes containing the doubly dendronised (two dendrons per ligand) poly(dendrimer) had a low turn on voltage of 3.6 V ($>1.0 \text{ cd m}^{-2}$), a maximum luminance of 6700 cd m^{-2} (at 12.2 V), and 100 cd m^{-2} was achieved at 6.0 V with an external quantum efficiency (EQE) of 9.2% (28.1 cd A^{-1}) and power efficiency of 14.7 lm/W . A solution of the doubly dendronised poly(dendrimer) in *N*-methyl-2-pyrrolidinone was found to have a viscosity of 4.6 mPa s , which falls in the range of solutions that can be inkjet printed.

Introduction

Since the discovery of thin film fluorescent organic light-emitting diodes (OLEDs),¹ step changes in the technology have relied on the development of new classes of materials. The first report of light-emitting polymers² brought the potential for large area solution-processed displays and lighting while the seminal papers on phosphorescent emitters^{3,4} opened the door to devices that can have internal quantum efficiencies approaching unity.^{5,6} The majority of work on phosphorescent materials has focused on small molecules,⁷ and in particular iridium(III) complexes that are processed by evaporation.⁸ An important step forward in the field was the discovery of solution-processable phosphorescent dendrimers that could form highly efficient devices with simple architectures.^{9–12} Attempts at combining light-emitting polymers with phosphorescent emitters have proved problematic as the triplet energy of many conjugated polymers is sufficiently low that they can quench the luminescence of the phosphorescent emitter, especially of green and blue emitters.^{13–16} Given the desire to print light-emitting devices it would be ideal to have materials that are solution processable, phosphorescent, highly luminescent, and with the viscosity

necessary for printing. Light-emitting dendrimers fulfill the first three criteria but not the last.

We have therefore focused on developing a new class of light-emitting material, namely poly(dendrimers) that have a non-conjugated backbone with dendrimer side-chains.^{17–20} While polymers with small molecule iridium(III) complex side-chains^{21–25} have been reported, the homopolymers have tended to have poor solubility^{24,26} and the complexity of copolymers leads to more difficult syntheses and issues relating to reproducibility. In our first reports on phosphorescent poly(dendrimers) that were comprised of dendrimer side-chains the dendrimers were comprised of heteroleptic iridium(III) complex cores. The cores had two 2-phenylpyridyl ligands with each having a single first generation biphenyl-based dendron with 2-ethylhexyloxy surface groups attached. The third ligand formed the connection point with the polymer backbone.^{17–20} The use of iridium(III) complexed dendrimer side-chains improved the solubility and enabled solutions with increased viscosity more suitable for printing to be made. However, their neat film photoluminescence quantum yields (PLQYs) were only 9–16%, which is too low for highly efficient simple OLEDs. Blending these polymers with a host enabled OLEDs with modest, $\sim 6\%$ external quantum efficiencies, to be fabricated.^{18–20}

In this manuscript we report a new design concept for poly(dendrimers) that has the potential to satisfy the requirements for printable, efficient host-free phosphorescent OLEDs. We have found that by increasing the number of dendrons on the dendrimer side-chain that intra- and interchain chromophore interactions can be controlled in the solid-state leading to films with

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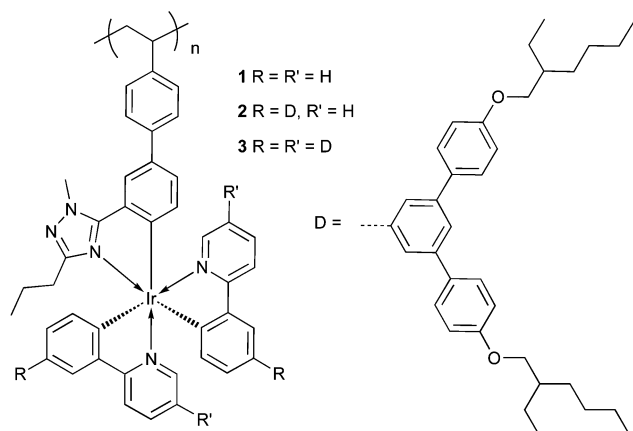


Fig. 1 Structures of homopolymer **1** and poly(dendrimers) **2** and **3**.

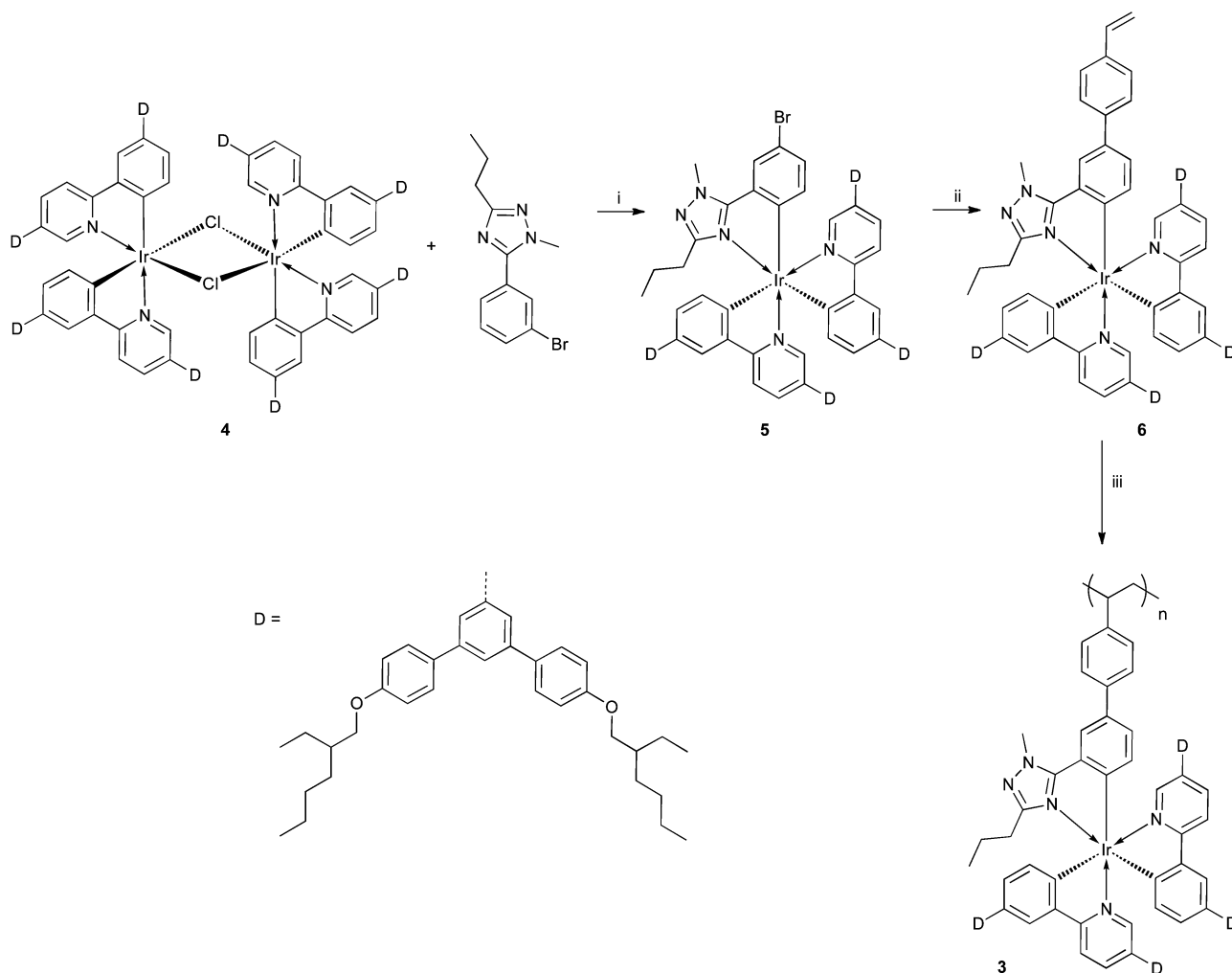
high PLQYs. In this work we compare the properties of the parent non-dendronised polymer (**1** in Fig. 1) with the 'mono-' **2** and the new 'doubly-' **3** dendronised materials and illustrate how molecular engineering can be used to optimise the optoelectronic and device properties.

Results and discussion

Synthesis and physical properties

The three polymers shown in Fig. 1 are homopolymers comprised of a poly(styrene) backbone to which an heteroleptic iridium(III) complex is attached. The iridium(III) complex in each case has two phenylpyridyl ligands and one phenyltriazolyl ligand, with the latter providing the attachment point to the polymer backbone. Poly(dendrimer) **2** differs from **1** in that it has a first generation biphenyl-based dendron with 2-ethylhexyloxy surface groups attached to each of the phenyl rings of the 2-phenylpyridyl ligands. Poly(dendrimer) **3** has dendrons attached in the same position as **2** plus an additional dendron on each of the pyridyl rings. The syntheses of **1**²⁵ and **2**¹⁹ have been previously reported.

The steps for the formation of poly(dendrimer) **3** are shown in Scheme 1. Poly(dendrimer) **3** was formed by the radical polymerisation of a styrene monomer. The styrene monomer was itself prepared *via* a convergent route with four key steps: the formation of the doubly dendronised 2-phenylpyridyl ligand²⁷ subsequent formation of the bis-chloro-bis-iridium dimer²⁷ reacting of the dimer with 5-(3-bromophenyl)-1-methyl-3-n-propyl-1*H*-[1,2,4]triazole²⁸ in the melt at 168 °C ($\approx 32\%$ yield),



Scheme 1 Reagents and conditions: (i) $\text{Ag}(\text{CF}_3\text{SO}_3)$, heat, Ar, 20 h; (ii) 4-vinylphenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, 2 M $\text{K}_2\text{CO}_3(\text{aq})$, EtOH, PhMe, reflux, Ar, 24 h; (iii) 1,1-azobis(cyclohexanecarbonitrile), *N*-methyl-2-pyrrolidinone, 80 °C, Ar, 24 h.

and a Suzuki coupling reaction with 4-vinylphenylboronic acid (91% yield). The styrene monomer was polymerized using 1,1-azobis(cyclohexanecarbonitrile) as the initiator and *N*-methyl-2-pyrrolidinone as the solvent at 80 °C, to give a bright yellow powder after purification by re-precipitation and size exclusion chromatography in a yield of 92% by mass. The molecular weight and polydispersity of poly(dendrimer) **3** was analysed by gel permeation chromatography (GPC) [against poly(styrene) standards] and an M_w of 2×10^4 and a polydispersity of 4 was found. However, it is important to note that in previous work it has been found that GPC can underestimate the molecular weight by a factor of around three to four,¹⁸ and hence the molecular weight is likely to be higher. Nevertheless, a high molecular weight polymer was not formed and this can be easily understood by the fact that the monomer is sterically hindered, which reduces the propagation rate relative to the termination processes. Poly(dendrimer) **3** exhibited good solubility in a variety of common organic solvents including tetrahydrofuran, dichloromethane, chloroform, toluene, 1,2-dichloroethane, and *N*-methyl-2-pyrrolidinone. In contrast, the non-dendronised homopolymer **1** was only soluble in a limited number of solvents such as dichloromethane and 1,2-dichloroethane,²⁵ illustrating that dendronisation significantly improves solubility. In addition, poly(dendrimer) **3** could be spin-coated to form good quality thin films. Given that one of the aims of the poly(dendrimer) design was to develop a dendrimer containing material that could have an increased viscosity relative to an isolated dendrimer we measured the kinematic viscosity as a function of concentration in 1,2-dichlorobenzene at 20 °C with the concentrations up to 100 mg cm⁻³. At a concentration of 25 mg cm⁻³ the viscosity of poly(dendrimer) **3** was found to be 1.35×10^{-6} m² s⁻¹ (1.35 cSt), which was 27% higher than the solvent viscosity (1.06×10^{-6} m² s⁻¹ for 1,2-dichlorobenzene), and also higher than the monomer from which **3** was made and **2** at the same concentration (the monomer and **2** had viscosities of 1.14×10^{-6} m² s⁻¹ and 1.23×10^{-6} m² s⁻¹, respectively in 1,2-dichlorobenzene at 25 mg cm⁻³). When the concentration of **3** was increased to 100 mg cm⁻³, the viscosity reached 2.10×10^{-6} m² s⁻¹. The viscosity of solutions can be strongly affected by the solvent and we found that by changing the solvent to *N*-methyl-2-pyrrolidinone a viscosity of 4.60×10^{-6} m² s⁻¹ was measured for poly(dendrimer) **3** at a concentration of 100 mg cm⁻³. That is, the poly(dendrimer) strategy is a successful method for increasing the solution viscosity of dendrimer-based materials. Piezoelectric inkjet printers commonly require inks with viscosities in the range 1–20 mPa s although there are reports on inkjet printed fluids with viscosities up to 30 mPa s.^{29,30} Assuming that the density of the polymer solutions are ≈ 1.0 g cm⁻³ then the measured kinematic viscosity for the 100 mg cm⁻³ solution of **3** in *N*-methyl-2-pyrrolidinone is equal to 4.6 mPa s and hence falls in the range of solutions that can be ink jet printed.

The first step in understanding the optoelectronic properties of poly(dendrimer) **3** was to determine the oxidation potential. Cyclic voltammetry (CV) showed poly(dendrimer) **3** underwent a single chemically reversible oxidation with an $E_{1/2}$ of 0.30 V with respect to the ferrocenium/ferrocene couple. Within experimental error this is at the same potential (0.28 V) as the monomer and shows that the close proximity of dendrimers along the polymer backbone did not significantly alter the

electronic properties of the iridium(III) complexes. This shows there are no strong intrachain interactions of the core complexes of the dendrimers, which are the electroactive chromophores.³¹

We next compared the optical properties of the materials. Fig. 2 shows the solution absorption spectra of poly(dendrimer) **3** in dichloromethane. The absorption spectra of iridium(III) complexed cored dendrimers are normally divided into two regions; the absorptions at wavelengths greater than 350 nm are assigned to the core iridium(III) complex and in particular to the metal-to-ligand charge transfer transitions whilst those at shorter wavelengths are primarily comprised of the π – π^* transitions of the ligands and the chromophores in the dendrons.³² Importantly, in moving from solution to the solid state the absorption spectrum of **3** was essentially the same (Fig. 2) showing that there is not strong aggregation of the core chromophores. This is consistent with the design of **3** whereby the doubly dendronised ligands comprised of biphenyl units in the dendrons and 2-ethylhexyloxy surface groups encapsulate the emissive complexes.

Fig. 2 also shows the normalized photoluminescence (PL) spectra of the three polymers in solution. The emission spectrum of poly(dendrimer) **3** had a peak at 551 nm and a shoulder at 588 nm. The emission of **3** is red shifted relative to poly(dendrimer) **2** (peak at 518 nm and a shoulder at 548 nm) and polymer **1**, which have very similar emission. The shift in emission colour for **3** is in line with our previous work that showed for phosphorescent dendrimers the attachment point of the dendrons has an effect on the emission properties of the material relative to the undendronised complex.³² When the dendron is attached to the ligand phenyl *meta* to the pyridyl ring it does not appreciably change the conjugation length of the ligand and hence the emission is similar to that of the parent complex thus explaining why the PL spectra of **1** and **2** are essentially the same (Fig. 2). However, when the dendron is attached either on the ligand pyridyl or phenyl rings in such a way that the π -delocalisation is increased then the emission is red shifted. This is the case for **3** where the branching phenyl ring of the dendron on the pyridyl ring is *para* to the ligand phenyl group. A key effect of having the second dendron on the ligand is that in the solid-state the PL spectrum is identical to that in solution strongly suggesting that the inter- and intra-polymer interchromophore interactions have been controlled.

The power of dendronisation to encapsulate and prevent detrimental interchromophore interactions was further exemplified by PL quantum yield (PLQY) measurements. The solution PLQY of homopolymer **1** was 23% and this low (relative to the parent small molecule complex which has a solution PLQY of 82%) PLQY was attributed to the fact that there were intrachain interchromophore interactions that led to the quenching of the luminescence. This explanation was supported by the fact that addition of a single dendron to each of the ligands of the complexes as in poly(dendrimer) **2** led to a large increase in the solution PLQY (61%). That is, the intrachain interchromophore interactions had been substantially reduced. As might be expected poly(dendrimer) **3** also has an excellent solution PLQY, which at 67%, is slightly higher than that of monodendronised poly(dendrimer) **2**. Nevertheless, the PLQYs of both **2** and **3** are both less than the 82% of the parent small molecule complex in solution indicating that there is still some level of intrachain interchromophore interactions in the polymer.

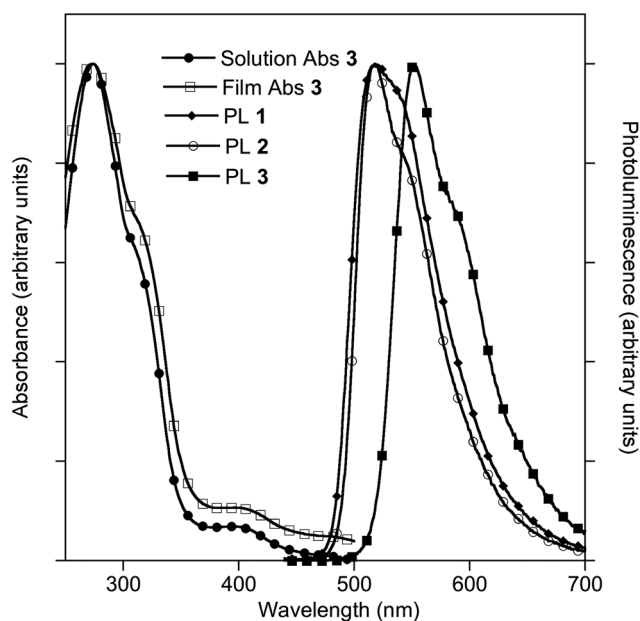


Fig. 2 Normalised UV-visible solution and film absorption spectra of poly(dendrimer) **3**. Also shown are the solution photoluminescence (PL) spectra in dichloromethane (excitation wavelengths: 310 nm for **1** and 360 nm for **2** and **3**), which are normalised at their peak maxima for ease of comparison.

Time-resolved PL measurements of the solutions confirmed these intrachain interchromophore interactions with the PL decay of poly(dendrimer) **3** having two components, 1.05 μ s (23%) and 1.83 μ s (77%), showing that there was more than one emissive environment. Significantly for application in OLEDs, in moving from solution to the solid-state the PLQY of neat films of poly(dendrimer) **3** remained high at 47%. This is in contrast to poly(dendrimer) **2** where the PLQY dropped from 61% in solution to 13% in the solid-state. That is, the use of double dendronisation controls both intra- and interchain interchromophore interactions. Increasing the generation of the doubly dendronised dendrimer side-chains would in principle enable further control over the intra- and interchain interactions. However, the increased steric bulk would almost certainly retard the polymerisation process.

Encouraged by the high film PLQY of poly(dendrimer) **3** in a neat film, hostless bilayer OLEDs were fabricated with 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) as an electron-transporting/hole-blocking layer. The OLED structure was ITO/poly(dendrimer) **3** (75 nm)/TPBI (60 nm)/LiF (0.7 nm)/Al (>100 nm) and the device properties are shown in Fig. 3. The devices had a low turn on voltage of 3.6 V (>1.0 cd m^{-2}), which indicates good charge-carrier injection despite the non-conjugated polymer backbone and the spacing provided by the dendrons. The maximum luminance of 6 700 cd m^{-2} was achieved at 12.2 V (Fig. 3a) and 100 cd m^{-2} was achieved at 6.0 V with an external quantum efficiency (EQE) of 9.2% (28.1 cd A^{-1}) and power efficiency of 14.7 lm/W . Importantly, the external quantum efficiency of the devices did not roll off quickly at higher brightnesses with an EQE of 8.4% (25.6 cd A^{-1}) at 1000 cd m^{-2} and 8.6 V, and EQE of 6.7% at 5000 cd m^{-2} and 11.4 V. These devices are superior to the OLEDs comprised of

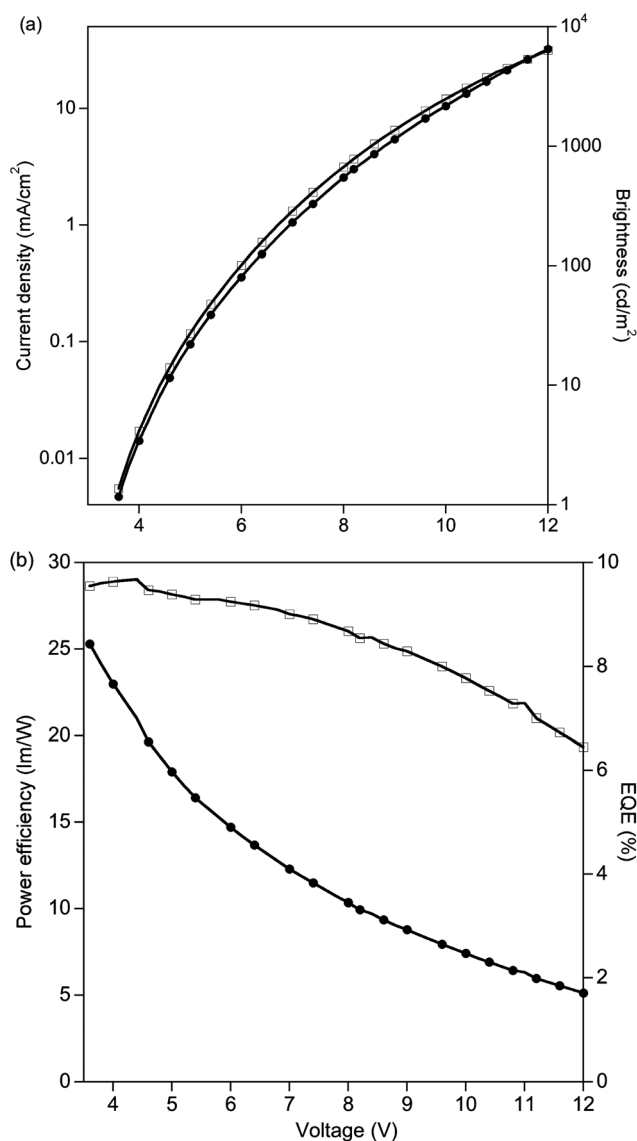


Fig. 3 Device characteristics of poly(dendrimer) **3** with the configuration of ITO/**3** (75 nm)/TPBI/LiF/Al: (a) current density-voltage-brightness characteristics (solid circles – current density, open-squares – brightness); (b) power efficiency-voltage-EQE characteristics (solid circles – power efficiency, open-squares – EQE).

poly(dendrimer) **2**, which had to be blended with CBP due its low neat film PLQY. The best bilayer devices with poly(dendrimer) **2** as a 20 wt% blend with CBP and the same TPBI electron transporting/hole blocking layer had a maximum EQE of 7.5% and at 100 cd m^{-2} (13.1 V) the EQE was 6.2% (21.8 cd A^{-1}) and the power efficiency was 5.2 lm/W .¹⁹ Finally, the poly(dendrimer) **3** film PL and electroluminescence spectra were identical (Fig. 4) with the C.I.E. co-ordinates being (0.48, 0.51), which corresponds to yellow emission.

Conclusions

In summary, we have demonstrated a very effective strategy for the design of highly efficient phosphorescent materials with

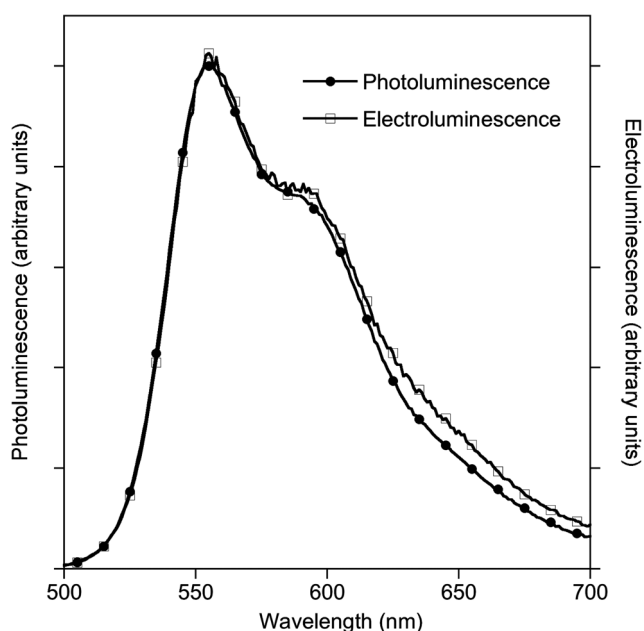


Fig. 4 Neat film photoluminescence and bilayer electroluminescence spectra of poly(dendrimer) **3**. The electroluminescence spectrum was collected at 12 V.

increased solution viscosity that can be used in host-free OLEDs. The fact that the PLQY was not greatly reduced in the solid-state compared to solution for poly(dendrimer) **3** shows that the 'double dendron' approach to controlling interchromophore interactions, which was effective for dendrimers,¹⁰ can also be used for poly(dendrimers). Importantly, the encapsulation of the dendrimer side-chain units does not inhibit charge transport in the films enabling the fabrication of simple bilayer devices with good efficiencies. Finally, the increased solution viscosity achievable with poly(dendrimers) makes them promising materials for printable OLEDs.

Experimental

Measurements

All commercial reagents were used as received unless otherwise noted. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere before use. ¹H and ¹³C NMR spectra were recorded using a 300 MHz or 400 MHz Bruker spectrometer, in deuterated chloroform; EH = 2-ethylhexyl, Pr = n-propyl, BPH = branch phenyl H, LH = ligand phenyl/pyridyl H, SPH = surface phenyl H, styrylPH = protons of the phenyl ring attached to the vinyl moiety, EtPH = protons of the phenyl ring attached to the polymer backbone, EtH = protons of the polymer backbone. All coupling constants (*J*) are in Hertz and quoted to the nearest 0.5 Hz. Gel permeation chromatography (GPC) was carried out using a 1515 Isocratic pump (Waters), a 717 autosampler (Waters), Styragel HT 6E and Styragel HT 3 columns (Waters) run in series, a 2487 Dual wavelength detector (Waters) set to 254 nm and 280 nm and a 2414 differential refractive index detector (Waters). Tetrahydrofuran was used as the mobile phase at a flow rate of 1 cm³ min⁻¹. Empower 2 (Waters) was used for data collection and

processing. For the determination of molar mass by conventional SEC, the columns were calibrated by polystyrene standards (Waters) covering the molar mass range of 1 060–1 320 000 g mol⁻¹. Microanalyses were carried out in Microanalysis Laboratory at School of Chemistry & Molecular Biosciences, the University of Queensland. UV-visible absorption measurements were recorded with a Cary Varian 5000 UV-Vis-NIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer STA6000. Mass spectra were recorded on an Applied Biosystems Voyager matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) from 2-[(2-*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) in positive reflection mode.

Viscosities of poly(dendrimer) **3** at different concentrations in 1,2-dichlorobenzene were determined on a home-made OST-WALD viscometer at a constant temperature of 20 °C. Deionised freshly distilled water with viscosity of 1.00 centistokes at 20 °C has been used as a reference.³³

Electrochemistry was performed using a BAS Epsilon electrochemistry station using a glassy carbon working, 0.1 M AgNO₃ in acetonitrile reference, and platinum counter electrodes. All measurements were made at room temperature on samples at a 1 mM concentration in dichloromethane (HPLC grade), with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as electrolyte. The solutions were deoxygenated with argon and the ferricenium/ferrocene (Fc⁺/Fc) couple was used as standard.³⁴ The scan rate was 100 mVs⁻¹ and in all cases several scans were carried out to confirm the chemical reversability of the redox processes.

Solution PLQYs were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid, which has a PLQY of 0.546, as the standard.³⁵ Materials were dissolved in dichloromethane and freeze-thaw degassed. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the solutions excited at 360 nm. The optical densities of the standard and sample were similar and small (~0.1). The accuracy of these measurements is estimated to be ±10% of the stated value. Time-resolved luminescence measurements were performed using the time-correlated single photon counting technique, with excitation at 393 nm from a pulsed Picoquant GaN laser diode and an instrument response of ~1 ns. Solid-state PLQY measurements were made using an integrating sphere purged with nitrogen³⁶ in a Hamamatsu C9920-02 measurement system.³⁷ Samples were excited at 325 nm. OLEDs were fabricated on ITO substrates that were etched using zinc powder and 37% hydrochloric acid. The ITO was cleaned by sonication in acetone and 2-propanol before oxygen plasma ashing for 5 min. Poly(dendrimer) **3** was spin-coated from a 10 mg cm⁻³ solution in dichloromethane at 2000 rpm. The devices were then placed in an evaporator operating at a pressure of 2 × 10⁻⁶ mbar and a 60 nm electron transporting/hole blocking layer of 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI), followed by a 0.7 nm thin layer of LiF and >100 nm aluminium cathode were deposited by thermal vapor deposition. OLEDs were characterised in vacuum using a Keithley 2400 Sourcemeter to measure IV characteristics and a calibrated photodiode to measure light emission in the forward direction. Total efficiency was calculated assuming Lambertian emission.

Synthesis of 5

A mixture of bis-iridium bis-chloro dimer **4**²⁷ (1.00 g, 0.20 mmol), 5-(3-bromophenyl)-1-methyl-3-n-propyl-1*H*-1,2,4-triazole²⁸ (566 mg, 2.02 mmol), and silver trifluoromethanesulfonate (207 mg, 0.81 mmol) was heated in an oil bath at 168 °C under argon for 20 h. The mixture was allowed to cool to room temperature and purified by column chromatography over silica using a dichloromethane/light petroleum mixture (1 : 1) as eluent to give **5** as an orange-red solid (346 mg, 32%); Found: C, 74.9; H, 7.7; N, 2.5%; C₁₇₀H₂₀₅BrIrN₅O₈ requires C, 75.1; H, 7.6; N, 2.6. λ_{\max} (CH₂Cl₂)/nm: 276 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (5.33)], 311sh (5.14), 391 (4.19), 473sh (3.64); ¹H NMR (400 MHz, CDCl₃): 0.51 (3 H, t, *J* = 7, Pr CH₃), 0.90–1.03 (48 H, m, EH CH₃), 1.27–1.63 (64 H, m, EH CH₂), 1.63–1.73 (2 H, m, Pr CH₂), 1.73–1.84 (8 H, m, EH CH), 1.88–2.11 (2 H, m, Pr CH₂), 3.75 (4 H, m, ArOCH₂), 3.87–4.00 (12 H, m, ArOCH₂), 4.22 (3 H, s, NCH₃), 6.78 (4 H, 1/2AA'BB', SPH), 6.94–7.13 (17 H, m, LPH, BPH, and/or SPH), 7.27–7.36 (2 H, m, LPH), 7.39–7.51 (11 H, m, LPH, BPH, and/or SPH), 7.54 (2 H, d, *J* = 1.5, LPH or BPH), 7.62–7.74 (12 H, m, LPH, BPH, and/or SPH), 7.74–7.81 (3 H, m, LPH or BPH), 7.83 (2 H, d, *J* = 1.5, LPH or BPH), 7.97–8.20 (6 H, m, LPH, and/or BPH), 8.41 (1H, s, LH); *m/z* [MALDI: DCTB]: Calcd for C₁₇₀H₂₀₅BrIrN₅O₈, 2714.5 (14%), 2715.5 (27%), 2716.5 (62%), 2717.5 (88%), 2718.5 (100%), 2719.5 (92%), 2720.5 (66%), 2721.5 (36%), 2722.5 (16%), 2723.5 (6%); Found, 2714.3 (13%), 2715.2 (17%), 2716.2 (61%), 2717.2 (82%), 2718.2 (100%), 2719.1 (89%), 2720.1 (68%), 2721.1 (33%), 2722.1 (16%), 2723.1 (7%). GPC: \bar{M}_w = 3 004; \bar{M}_n = 3 001; polydispersity = 1.0. Excess ligand (320 mg), which co-chromatographed with and had an identical ¹H NMR to an authentic sample, was also recovered. $E^{1/2}(\text{ox})$ = 0.31 V vs. Fc⁺/Fc.

Synthesis of 6

A mixture of **5** (340 mg, 0.12 mmol), 4-vinylphenylboronic acid (46.3 mg, 0.31 mmol), tetrakis(triphenylphosphine)palladium(0) (14.5 mg, 0.01 mmol), aqueous potassium carbonate (2 M, 0.63 cm³), ethanol (0.63 cm³), and toluene (2 cm³) was deoxygenated (by placing under vacuum and backfilling with argon three times) and then heated at reflux under argon for 24 h. The mixture was allowed to cool to room temperature and then water (30 cm³) and dichloromethane (10 cm³) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 30 cm³). The organic portions were combined and dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane/light petroleum mixtures (1 : 1) as eluent to give **6** as an orange-red solid (311 mg, 91%); Found: C, 77.7; H, 7.8; N, 2.6; C₁₇₈H₂₁₂IrN₅O₈ requires C, 78.0; H, 7.8; N, 2.55%. λ_{\max} (CH₂Cl₂)/nm 276 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (5.42)], 312sh (5.25), 396sh (4.33), 483sh (3.64); ¹H NMR (400 MHz, CDCl₃): 0.55 (3 H, t, *J* = 7, Pr CH₃), 0.90–1.10 (48 H, m, EH CH₃), 1.30–1.65 (64 H, m, EH CH₂), 1.66–1.75 (2 H, m Pr CH₂), 1.75–1.90 (8 H, m, EH CH), 1.96–2.15 (2 H, m, Pr CH₂), 3.77 (4 H, m, ArOCH₂), 3.89–3.98 (12 H, m, ArOCH₂), 4.31 (3 H, s, NCH₃), 5.27 (1 H, d, *J* = 11, VinylH), 5.81 (1 H, d, *J* = 17.5, VinylH), 6.75–6.83 (5 H, m, VinylH and SPH), 6.97–7.15 (14 H, m, LH,

BPH, styrylPH, and/or SPH), 7.20–7.30 (3 H, m, LH), 7.36 (2 H, dd, *J* = 8.5, *J* = 8.5, LH), 7.43–7.55 (12 H, m, BPH, SPH, styrylPH, and/or LH), 7.58–7.66 (4 H, m, SPH, BPH, styrylPH, and/or LH), 7.66–7.90 (17 H, m, SPH, styrylPH, BPH, and/or LH), 8.01–8.25 (6 H, m, BPH and/or LH), 8.52 (1 H, s, LH); *m/z* (MALDI:DCTB): Calcd for C₁₇₈H₂₁₂IrN₅O₈: 2738.6 (21%), 2739.6 (42%), 2740.6 (80%), 2741.6 (100%), 2742.6 (87%), 2743.6 (55%), 2744.6 (27%); Found: 2738.7 (29%), 2739.7 (56%), 2740.6 (90%), 2741.6 (100%), 2742.5 (80%), 2743.3 (51%), 2744.3 (24%). GPC: \bar{M}_w = 2 980; \bar{M}_n = 2 978; PD = 1.00 (a small peak was also detectable with \bar{M}_w = 5 559, \bar{M}_v = 5 555 and polydispersity = 1.00, which was attributed to the dimer structure of **4**). $E^{1/2}(\text{ox})$ = 0.28 V vs. Fc⁺/Fc.

Poly(dendrimer) 3

6 (1.2 g, 0.4 mmol), 1,1-azobis(cyclohexanecarbonitrile) (2.14 mg, 0.01 mmol), and *N*-methyl-2-pyrrolidinone (1.0 cm³) were placed in a Schlenk tube. The mixture was deoxygenated by cooling in a dry ice bath, and then placing under vacuum and backfilling with argon three times. The reaction mixture was then heated at 80 °C for 24 h before being allowed to cool to room temperature. The reaction mixture was then diluted with tetrahydrofuran (5 cm³) before being dropped into methanol (50 cm³) that was being stirred. The precipitate was collected at the filter and the precipitation procedure was repeated twice more. The precipitate was collected and further purified by size exclusion chromatography over Sephadex using tetrahydrofuran as the solvent. The solvent was removed and residue dried to give a bright yellow powder of **3** (1.1 g, 92%). Found, C, 77.6; H, 7.7; N, 2.55; (C₁₇₈H₂₁₂IrN₅O₈)_n requires C, 78.0; H, 7.8; N, 2.55. λ_{\max} (CH₂Cl₂)/nm 273, 313sh, 400sh, 482sh; ¹H NMR (300 MHz, CDCl₃): 0.40–2.20 (120 H, brm, Pr CH₂ and Pr CH₃, EtH, EH CH₂, EH CH₃, and EH CH), 3.10–4.40 (19H, brm, ArOCH₂ and NCH₃), 6.20–8.50 (63 H, brm, SPH, BPH, EtPH, and LH); GPC: \bar{M}_w = 2 × 10⁴, \bar{M}_n = 5 × 10³, polydispersity = 4. $E^{1/2}(\text{ox})$ = 0.30 V vs. Fc⁺/Fc. TGA: (scan rate = 10 °C min⁻¹, weight = 1.068 mg) 5% weight loss at 387 °C.

Acknowledgements

P.L.B. is recipient of an Australian Research Council Federation Fellowship (Project No. FF0668728). J.W.L and I.D.W.S are grateful to the Engineering and Physical Sciences Research Council (UK) for financial support. WYL's current address is Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210046, China. This work was carried out in part at the Queensland node of the Australian National Fabrication Facility, a company established under the national collaborative research infrastructure strategy to provide nano- and micro-fabrication facilities for Australia's researchers.

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