

# Light-emitting poly(dendrimer)s

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## ABSTRACT

Organic light-emitting diodes (OLEDs) have great potential for displays and lighting applications. For large area displays the ideal materials would be both phosphorescent and solution processible. These requirements mean that the materials need to be able to be patterned and the most advanced method for forming pixelated displays is inkjet printing. Light-emitting phosphorescent dendrimers have given high efficiency monochrome displays with the emitting layer deposited by spin-coating. However, the viscosity of the dendrimer solutions is insufficient for inkjet printing. We report the development of a new class of light-emitting materials, namely poly(dendrimers) in which a green emissive phosphorescent dendrimer is attached to a poly(styrene) backbone. Free radical polymerization of a dendrimer-styrene monomer gave a poly(dendrimer) with a weight average molecular weight of 24000 and a polydispersity of 3.6. A dilute solution of the dendrimer had a viscosity 15% higher than the neat solvent. Comparison of the photophysical studies of the poly(dendrimer) *versus* a model monomer dendrimer showed that the PL spectrum was broader and red-shifted, and the PL quantum yield around 50% lower. This was attributed to intermolecular interactions of the emissive dendrimers, which are held closely together on the polymer backbone.

**Keywords:** Dendrimer, poly(dendrimer), OLED, phosphorescence.

## 1. INTRODUCTION

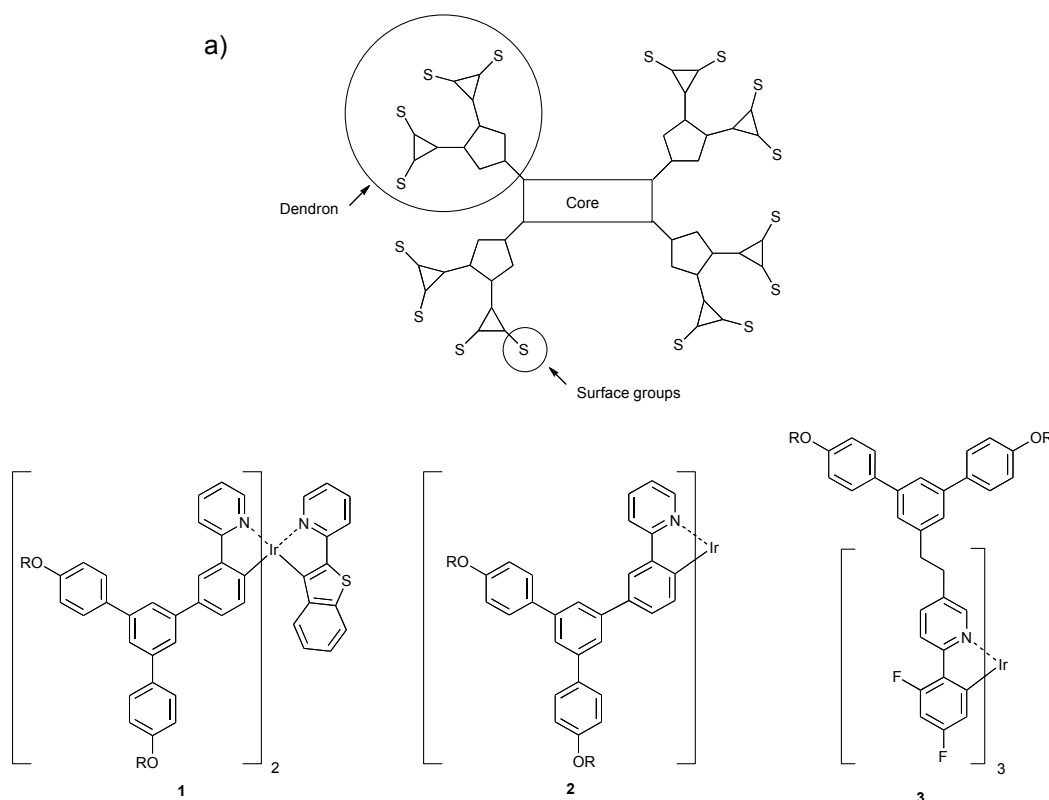
Organic light-emitting diodes (OLEDs) are of great interest for use in flat panel displays and lighting<sup>1,2</sup>. Driving their development for displays is the fact that they have wide viewing angles, can form very thin devices, have low power consumption and in the longer term can potentially be used in flexible screens. There are three classes of light-emitting materials that have been developed for OLEDs, namely small molecules<sup>3</sup>, polymers<sup>4</sup>, and more recently dendrimers<sup>5</sup>. Small molecule light-emitting materials are processed into displays by vacuum vapour deposition. However, the vacuum vapour deposition process is relatively expensive in terms of materials as the masking process means that only a third of the material is used in the production of a full colour display with the remaining material wasted. Nevertheless, the most advanced commercial displays are based on small molecule technologies. However, for large area displays and more efficient use of the light-emitting materials it would be better to be able to place the light-emitting material only where it is needed during the manufacturing process. Light-emitting polymers are processed from solution. While spin-coating can provide simple monochrome devices much effort has been put into inkjet printing techniques for the formation of solution processed pixelated full colour displays. The use of inkjet printing gives rise to the possibility of large area devices in combination with efficient use of the light-emitting material as it is only placed in the desired pixel<sup>6</sup>. One problem with light-emitting polymers is that they are fluorescent rather than phosphorescent so that there are substantial losses due to triplet formation. One method for overcoming this is to blend a phosphorescent emitter with or attach it to a conjugated polymer<sup>7</sup>. While this has been successful for combinations of red phosphorescent emitters and blue emissive

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conjugated polymers the relatively low triplet energies of many conjugated polymers means that this strategy will be more difficult for green and blue phosphorescent materials. Light-emitting dendrimers are the third class of materials that have been developed for OLEDs. Both fluorescent and phosphorescent dendrimers have been prepared with the latter giving rise to simple highly efficient devices<sup>8-10</sup>.

Light-emitting dendrimers are monodisperse macromolecular structures consisting of a core, dendrons, and surface groups (Figure 1). By carefully choosing each of these components, the light emitting properties, morphology, and solubility can be controlled independently. For example, phosphorescent dendrimers with different iridium(III) complex cores [(1), (2), and (3) (Fig. 1) give red<sup>11</sup>, green<sup>12</sup>, and sky blue<sup>13</sup> emission respectively], biphenyl-based dendrons, and 2-ethylhexyloxy surface groups have all given rise to efficient OLEDs<sup>14-16</sup>. However, thus far all the reported dendrimer devices have been fabricated by spin-coating from solution leading to monochrome displays. Given the excellent efficiencies of devices based on phosphorescent dendrimers it is therefore of interest to develop methods for the formation of pixelated displays. Clearly one method for forming patterned films would be to inkjet print the phosphorescent dendrimers. However, inkjet printing requires a minimum solution viscosity of around 1 mPas<sup>17</sup>, and dendrimer solutions typically have viscosities similar to the neat solvents, which are less than this. For example, toluene and chlorobenzene have viscosities of 0.56 mPas and 0.75 mPas, respectively. One method of increasing the viscosity of dendrimer-based materials would be to attach them to a polymer backbone. There have been a number of reports of polymers with small molecule phosphorescent materials attached to flexible polymer backbones<sup>18</sup>, but not of dendrimers attached to a polymer backbone. The polymers generally contain a heteroleptic iridium(III) complex in which the complex is attached to the backbone via an acetylacetonato ligand<sup>19</sup>.



In this manuscript we describe the method for forming the first light-emitting phosphorescent poly(dendrimer) (Figure 2). The poly(dendrimer) (**4**) consists of a heteroleptic complex that has two 2-phenylpyridyl ligands to which first generation biphenyl-based dendrons with 2-ethylhexyloxy surface groups are attached, and a pyridyltriazolyl coligand, which provides the attachment point to the polystyrene backbone. The combination of the two 2-phenylpyridyl and the pyridyltriazolyl ligands were used to ensure that the poly(dendrimer) emitted green light. In addition, we discuss the effect of the polymerization on the viscosity of the material in solution, and report the preliminary photophysical properties of the material.

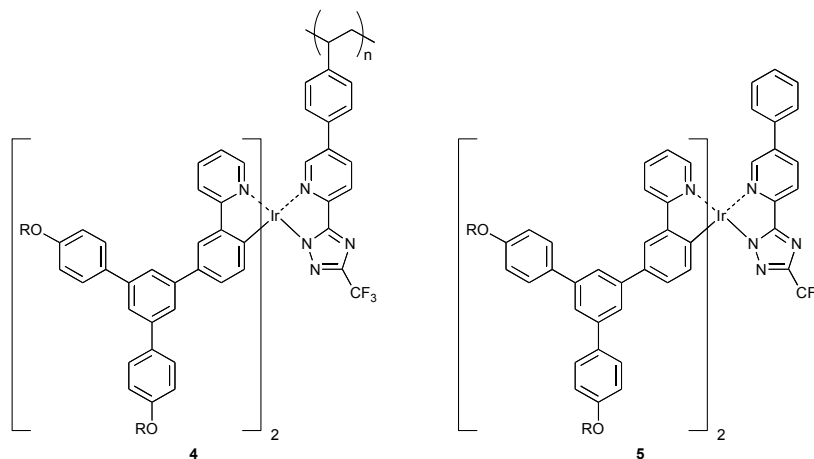
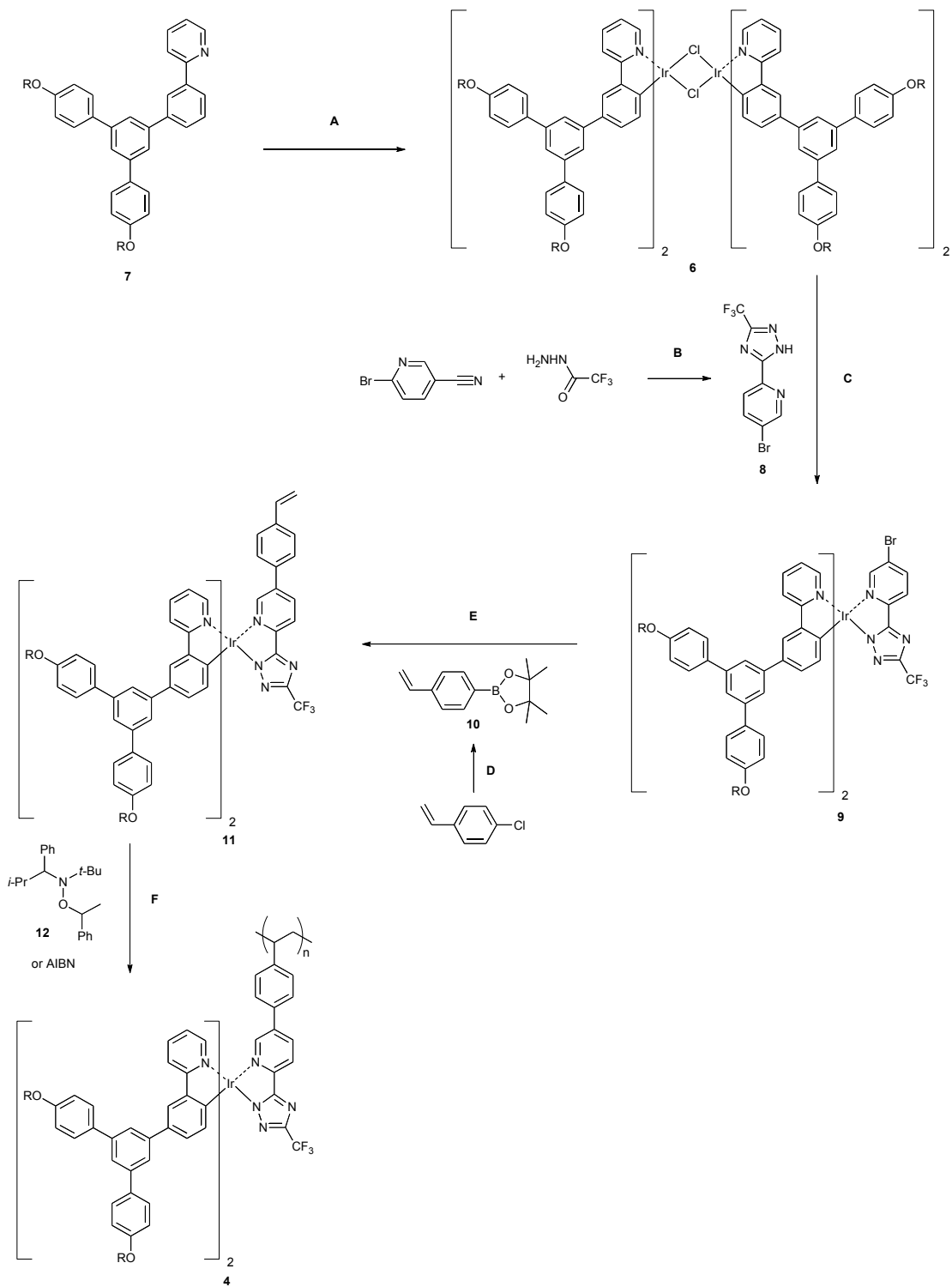


Figure 2. Target poly(dendrimer) (**4**) with two 2-phenylpyridyl ligands to which first generation biphenyl-based dendrons with 2-ethylhexyloxy surface groups are attached, and a pyridyltriazolyl coligand, which provides the attachment point to the polystyrene backbone and comparable dendrimer (**5**) on which the poly(dendrimer) (**4**) is based.

## 2. RESULTS

The strategy for the synthesis of the poly(dendrimer) is outlined in Scheme 1. The key intermediate was the *bis*-iridium *bis*-chloro dimer ( $[\text{G1-ppy}_2\text{IrCl}]_2$ ) (**6**), which was first isolated and used for the formation of **1**<sup>20</sup>. Briefly the *bis*-iridium *bis*-chloro dimer **6** was prepared by reaction of four equivalents of G1-ppy (**7**)<sup>21</sup> with iridium (III) chloride trihydrate in a 2-ethoxyethanol/water mixture heated at 130 °C. Crude  $[\text{G1-ppy}_2\text{IrCl}]_2$  (**6**) precipitated from the reaction mixture and so was easily collected by filtration before further purification by chromatography. In the preparation of **1** it has been shown that the dimer can be “cracked” with (hetero)arylpyridyl ligands although the relatively harsh conditions employed caused some ligand scrambling<sup>22</sup>. In contrast, pyridyltriazole ligand has been shown to “crack” *bis*-iridium *bis*-chloro small molecule dimers<sup>23</sup> under relatively mild conditions without scrambling.



Scheme 1: (A)  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ , 2-ethoxyethanol, 130 °C, 2 d (B) toluene, 130 °C, 60 h (C)  $\text{CHCl}_3$ , dark, rt, 3 h (D) i. THF, Mg,  $\Delta$ , 16 h ii. -78 °C, *iso*-propoxypinacolborane, -78 °C to rt (E) THF, vinylboronate ester (**10**),  $\text{Na}_2\text{CO}_3(\text{aq})$ ,  $\text{Pd}(0)[\text{PPh}_3]_4$ , dark, 76 °C, 15 h (F) *tert*-butyl benzene, nitroxide initiator (**12**) 130 °C, 72 h or *tert*-butyl benzene, AIBN, 140 °C, 16 h. (R = 2-ethylhexyl)

However, to enable the attachment of the styrene moiety required for the formation of the polymer backbone, it was necessary to produce the bromide-functionalised coligand **8**. 2-Bromo-2-cyanopyridine and trifluoroacetic acid hydrazide were reacted at 130 °C in a sealed tube to give the pyridyltriazolyl coligand **8** in a 28 % yield. In addition to the desired **8** a second product was also isolated, which is believed to be either the *N*-amide or *N*-oxide. The [G1-ppy<sub>2</sub>IrCl]<sub>2</sub> dimer (**6**) was then reacted with the bromide functionalised coligand **8** at room temperature in the dark with chloroform as the solvent. Under these very mild conditions the heteroleptic dendritic complex **9** was formed and isolated in a 39 % yield. Of the eight possible isomers that could theoretically be formed two distinct isomers were observed in an approximate ratio of 10:1 (determined from the ratio of peak heights in the <sup>19</sup>F), these were believed to be (**8A**) and (**8B**) (Figure 3) and their enantiomers, due to the known propensity of phenylpyridyl ligands to form *facial* isomers.

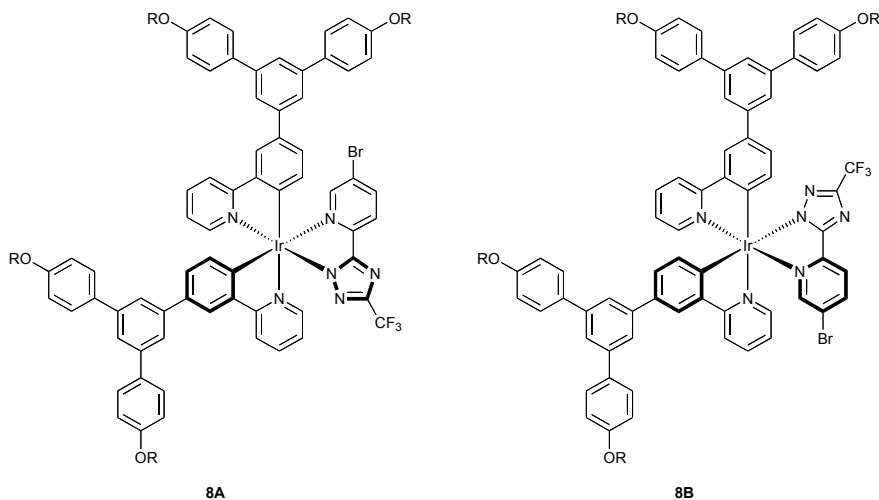


Figure 3. Quasi-facial isomers (**8A**) and (**8B**) of (**8**). (R=2-ethylhexyl)

To complete the synthesis of the monomer it was necessary to prepare the 4-vinylphenylboronate ester **10** for coupling to the bromo moiety on the pyridyltriazole ligand. The boronate ester was chosen over the corresponding boronic acid to allow for simpler purification and to avoid any possibility of cationic polymerization. The 4-vinylphenylboronate ester **10** was reliably formed by reaction of 4-chlorostyrene with magnesium to give the Grignard reagent and then subsequent reaction with *iso*-propoxypinacolborane. Under these conditions vinylboronate ester (**10**) was isolated in a yield of 72%. Attempts to synthesise this compound from the Grignard of 4-bromostyrene were unsuccessful, leading to polymerisation, we believe that this may be due to the increased radical character of the bromo Grignard. The final step in the monomer synthesis was the Suzuki coupling of the 4-vinylphenylboronate ester **10** to the heteroleptic dendritic complex **9**. For this Suzuki reaction to work well it was necessary to use keep the temperature below 100 °C to avoid the autopolymerisation of the styrene<sup>24</sup>. In this work this was achieved by using tetrahydrofuran as the solvent, and the monomer **11** was formed in a 69 % yield.

It is known that the presence of vinyl units can quench the luminescence of phosphorescent emitters<sup>25</sup> and hence it was of interest to see what affect the styryl group had on the emissive properties of the monomer. The photoluminescence quantum yield (PLQY) of monomer (**11**) was measured as 1.5 % in degassed tetrahydrofuran. To confirm that this low PLQY value was due to the presence of a double bond the PLQY of **5**, which does not have the vinyl group, was prepared by reaction of bromofunctionalised dendrimer **9** with benzene boronic acid under Suzuki conditions to give (**5**) in an 89% yield. The PLQY of **5** was found to be 43%. The lowering of the PLQY by the styrene was not a great concern, as the polymerisation process leads to the removal of the double bond.

Polymerisation of styrene can be achieved under cationic, anionic, or radical conditions. For this work radical conditions were chosen. By using nitroxide initiators it is possible to polymerise styrene under living conditions to give rise to polymers with low polydispersity. Hence our first approach to forming the poly(dendrimer) was to use a nitroxide initiator. The nitroxide initiator **12** for the polymerisation of **11** was prepared according to a literature procedure<sup>26</sup>.

Nitroxide initiator **12** was chosen for its general application – specifically its ability to polymerise a range of monomers, including various styrenes. In the literature, bulk (no solvent) polymerisations using this initiator yielded specific molecular weights and narrow polydispersities *via* a pseudo living mechanism. However, in our case bulk polymerisations of the heteroleptic dendritic monomer was not possible, as it did not have a sufficiently low melting point. Therefore, the polymerisation of the heteroleptic dendritic monomer **11** was carried out at concentration of 0.18 M in *tert*-butylbenzene. Nitroxide initiator (**12**) was added (1 mol%) and the polymerisation was allowed to proceed at 130 °C for 72 hours. A green emissive material was isolated and the NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F) were found to all have broader peaks than the monomer indicating that a higher molecular weight material had been formed. Gel permeation chromatography (GPC) analysis against polystyrene standards gave the weight average molecular weight ( $\overline{M}_w$ ) as 8000 and a polydispersity of 1.8. The ( $\overline{M}_w$ ) of 8000 corresponds to a short chain of only a few units. Nevertheless we measured the viscosity of the oligomer in chlorobenzene at 20 °C and a concentration of 5.0 mg per mL and found it to be 0.76 mPas. This is a similar viscosity to neat chlorobenzene and it was therefore necessary to make poly(dendrimer)s of a longer chain length.

In an effort to achieve higher molecular weights two changes were made to the synthetic procedure; first, the concentration of the polymerization was increased, and second, an unmediated free radical polymerisation initiated by azobis(*iso*-butyronitrile) (AIBN) was used. It was recognized that the use of AIBN would likely lead to higher polydispersities but the ability to form a higher molecular weight simply was the key factor for its use. Iridium(III) complex-cored dendritic monomer **11** was dissolved in the minimum amount of *tert*-butylbenzene giving a concentration of 0.28 M and AIBN (1 mol%) was added. The polymerisation was allowed to proceed at 140 °C for 16 hours, yielding a green luminescent compound. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR confirmed the formation of a polymer with significant peak broadening occurring with respect to the monomer **11**. GPC analysis gave the molecular weight ( $\overline{M}_w$ ) as 24,000, giving an approximate chain length of 14 units with a polydispersity of 3.6. The viscosity of the polymer in chloroform solution at 20 °C and a concentration of 5.0 mg per mL was 0.83 mPas. This increase in solution viscosity is promising but not yet sufficient for inkjet printing.

The final part of this study was to determine the effect of the polymerization on the photophysical properties of the emissive dendrimer. The absorption spectra of the model compound **5** and the poly(dendrimer) **4** are shown in Figure 4. It can be seen that the model compound **5** and the poly(dendrimer) (**4**) both have similar UV-visible absorbances with weak long wavelength (>330 nm) absorptions that are due to the nominally ‘metal-to-ligand charge transfer’ (MLCT) transitions, and strong short wavelength absorptions at less than 330 nm due to the ligand  $\pi$ - $\pi^*$  transitions and dendron absorptions.

The photoluminescence spectra of the model compound **5** and the poly(dendrimer) **4** are shown in Fig. 5. It can be seen that **5** and the poly(dendrimer) **4** have different photoluminescence (PL) spectra. The poly(dendrimer) has a broader emission that is red-shifted. When comparing the difference between solution and film PL spectra a red-shift in the PL peak and a long red tail is indicative of strong intermolecular interactions of the emissive chromophores. For **5** the measurements are carried out in dilute solution and hence there are no intermolecular interactions of the emissive cores. In contrast although the solution of the poly(dendrimer) **4** is dilute the PL emission is reminiscent of interacting chromophores in the solid-state. This can be understood by the fact that the polymer backbone holds the dendrimers close together, even in solution. As stated earlier the PLQY of the simple model compound **5** with phenyl group on the pyridyl ring was 43% while that of the monomer was only 1.5%. The PLQY of the poly(dendrimer) **4** as a dilute solution in degassed toluene was 18%. The lower PLQY of **4** when compared to the model compound **5** is likely to primarily due to the inter-chromophore interactions of the emissive chromophores due to them been held closely to each other on the polymer backbone. Although the presence of small number of vinyl groups formed during termination reactions could also contribute, it would not explain the difference in the emission spectrum between **4** and **5**.

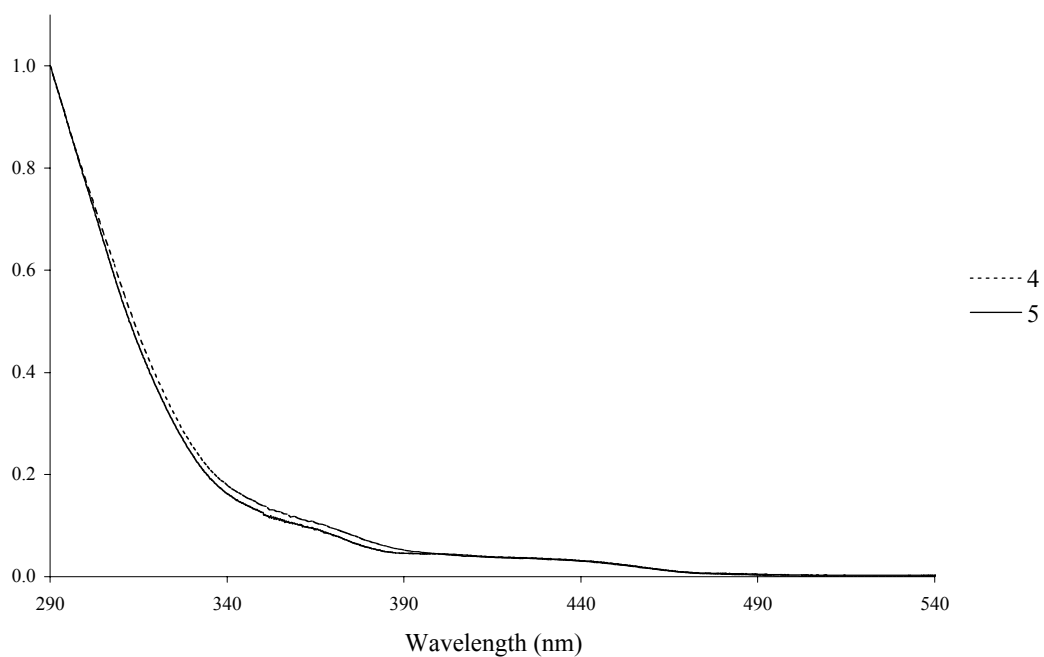


Figure 4. Normalised solution UV-visible absorption spectra of **4** and **5** in toluene.

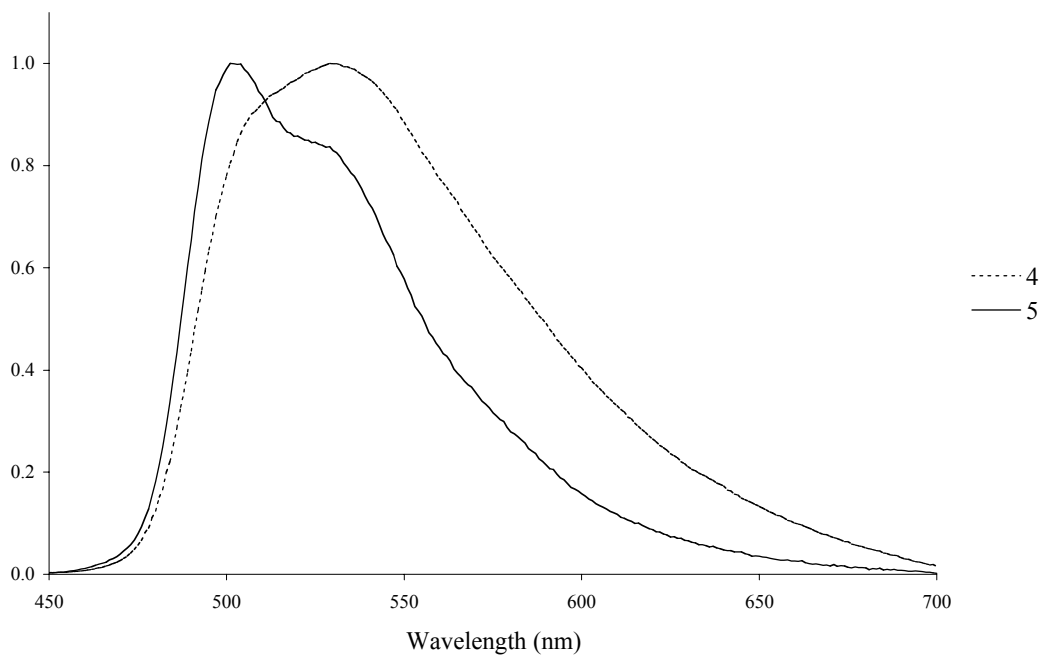


Figure 5. Solution photoluminescence spectra of **4** and **5**. The solutions (in toluene) were excited at 360nm and have been normalised for clarity.

### 3. CONCLUSION

We have developed the first green emissive phosphorescent poly(dendrimer)s, which have a polystyrene backbone. In this work it was found that due to having to carry out the polymerization in solution the use of a nitroxide mediated 'living' polymerization did not give the control to form a monodisperse polymer. A simple free radical polymerization using AIBN as an initiator gave a higher molecular weight poly(dendrimer). Importantly, the polymerization of the dendrimers led to increased solution viscosities. The solution PLQY of the poly(dendrimer) **4**, at 18 %, was lower than the model monomer and the PL spectra strongly suggested that this was due to interactions of the emissive chromophores, which are held at defined and close positions by the polymer backbone.

### 5. EXPERIMENTAL

Where appropriate dry glassware, solvents and inert atmosphere conditions were used and solvents were dried over activated alumina in a Grubb's column. Inert atmosphere is nitrogen unless otherwise stated. Thin layer chromatography was performed on Merck aluminium plates coated with silica gel 60 F<sub>254</sub>. Column chromatography was performed using the flash chromatography technique with Sigma Aldrich silica gel 230–400 mesh, 40Å. When solvent mixtures are used, their proportions are given by volume. Light petroleum refers to the fraction with boiling point 40–60 °C. All elemental analyses were carried out by Mr. S. Boyer at London Metropolitan University. UV-visible spectra were recorded on a Perkin Elmer UV lambda 14P spectrometer and as solutions in dichloromethane. Infrared spectra were recorded on a Bruker Tensor 27 Infrared spectrometer by pressing KBr discs. Values of absorption maxima are reported in wavenumbers (cm<sup>-1</sup>). <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F spectra were recorded on Bruker AV400, Bruker DPX400, or Bruker AV500 spectrometers. Chemical shifts (δ) are in parts per million (ppm) and are referenced to the residual solvent peak. The following abbreviations are used to describe multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, (J) are reported in Hertz (Hz) to the nearest 0.5 Hz. MALDI–TOF spectra were obtained from the Waters centre in Manchester on a Waters Micromass MALDI Micro MX mass spectrometer, in positive reflection mode, values for m/z are quoted in Daltons (Da). Gel Permeation Chromatography was carried out using a Polymer Laboratories PLGel Mixed-A column (600 and 300 mm lengths, 7.5 mm diameter), calibrated with poly(styrene) narrow standards, in tetrahydrofuran. The tetrahydrofuran was degassed with helium and pumped at a rate of 1 mL/minute at 30.0°C with a UV-visible detector set at 254 nm. Results were analysed with Polymer Laboratories CIRRUS software. Viscosity measurements were carried out using an Ostwald Viscometer 7985 in a Haake GH Fissions constant temperature bath at 20 °C using water as calibrant. Solution photoluminescence quantum yields (PLQYs) were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid which has a photoluminescence quantum yield of 0.546 as the standard<sup>27</sup>. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the dendrimer solutions excited at 360 nm.

#### **2-(5-Trifluoromethyl-2-H-1,2,4-triazolyl)-5-bromopyridine 8**

2-Bromo-2-cyanopyridine (1.00 g, 5.5 mmol) and trifluoroacetic acid hydrazide (1.30 g, 10.2 mmol) were dissolved in toluene (4 mL) in a sealable tube. The mixture was deoxygenated by 3 pump-fill (nitrogen) cycles and then the tube sealed and the reaction heated at 130 °C for 60 hours. The reaction was allowed to cool to room temperature and diethyl ether (20 mL) and water (20 mL) were added. The layers were separated and the organic layer was washed with water (2 × 20 mL), dried over magnesium sulfate, filtered, and the solvent removed. The resultant crude product was purified by column chromatography over silica using a dichloromethane:ethylacetate (19:1) mixture as eluent to give **8** (0.45 g, 28%): λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>)/nm 254 (log ε/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> 4.23), 288 (4.08) and 295sh; ν<sub>max</sub>/cm<sup>-1</sup> 3425, 1646, 1440, 1206, 1145 and 1023; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 8.12 (1H, m, CHCHCBr), 8.18 (1H, d, J = 8, CHCHCBr), 8.86 (1H, d, J = 2, NCH); δ<sub>C</sub>(125 MHz; CDCl<sub>3</sub>) 118.97 (q, J = 2.15, CF<sub>3</sub>), 123.31, 123.53, 140.72, 143.16, 150.97, 154.79, 155.27 (q, J = 0.32, CCF<sub>3</sub>); δ<sub>F</sub>(377 MHz; CDCl<sub>3</sub>) -65.40; m/z (EI) 293 ([M{<sup>81</sup>Br} – H]).

#### **[Bis-(2-{3-[3,5-bis(4-{2-ethylhexyloxy}phenyl)phenyl]phenyl}pyridyl)-2-(5-trifluoromethyl-2-H-1,2,4-triazolyl)-5-bromopyridyl]iridium(III) 9**

**6** (200 mg, 0.066 mmol) and **8** (60 mg, 0.204 mmol) were dissolved in chloroform (12 mL) and stirred for 3 hours in the dark, and then the solvent removed. The residue was purified by column chromatography over silica using dichloromethane:ether (1:0 → 97:3) mixtures as eluent to give **9** (90.7 mg, 39%): λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>)/nm 275 (log ε/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> 5.05); ν<sub>max</sub>/cm<sup>-1</sup> 3425, 1646, 1512, 1477, 1207, 1145 and 1000; δ<sub>H</sub>(400 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 0.91 – 1.04 (24H, m, Me), 1.34 – 1.75 (32H, m, CH<sub>2</sub>), 1.82 (4H, m, C<sub>3</sub>CH), 3.97 (8H, m, CH<sub>2</sub>O), 6.52 (1H, d, J = 8, *phpy*), 6.59 (1H, d, J = 8,



*phpy*), 7.00 – 7.15 (10H, m, CHCO and *phpy*), 7.31 (1H, d, *J* = 8, *phpy*), 7.39 (1H, d, *J* = 8, *phpy*), 7.7 – 8.3 (25H, m, ArH);  $\delta_{\text{C}}$ (125 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 11.30, 14.28, 23.49, 24.27, 29.49, 30.92, 39.85, 71.02, 115.19, 115.25, 119.91, 119.98, 120.06, 121.57, 122.06, 123.08, 123.84, 123.93, 123.98, 124.17, 124.37, 128.59, 129.37, 129.87, 130.41, 132.43, 132.97, 133.70, 133.76, 135.66, 136.05, 137.87, 138.19, 142.10, 142.18, 142.29, 142.41, 142.50, 142.88, 143.19, 144.76, 145.75, 145.98, 147.63, 149.21, 150.32, 150.57, 151.21, 152.00, 156.34, 156.63, 159.63, 159.69, 159.79, 163.60, 168.11, 168.20;  $\delta_{\text{F}}$ (377 MHz; CD<sub>2</sub>Cl<sub>2</sub>) -63.74 (100 %), -63.32 (10); *m/z* (MALDI-TOF) 1766 ([M + H]<sup>+</sup>, 100%), 1474 ([M – triazole ligand + H]<sup>+</sup>, 54).

### 2-[4-Vinylphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 10

To a stirred suspension of magnesium (105 mg, 4.32 mmol) in tetrahydrofuran (15 mL) was added 1,2-dibromoethane (1 drop) and then 4-chlorostyrene (0.42 mL, 3.6 mmol) was added dropwise. The mixture was then heated at reflux for 16 hours and subsequently cooled to -78 °C. Diethyl ether (25 mL) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.84 mL, 7.2 mmol) were added, and the solution allowed to warm to room temperature over 6 hours. Diethyl ether (50 mL) and water (50 mL) were added and the layers were separated. The organic layer was washed with water (2 × 50 mL), dried over sodium sulfate, filtered and the solvent removed *in vacuo*. This crude material was purified by flash column chromatography over silica using light petroleum:diethyl ether (1:0 → 0:1) mixtures as eluent to give **10** (592 mg, 72%), which had identical <sup>1</sup>H and <sup>13</sup>C NMR spectra to the literature<sup>28</sup>.

### [Bis-(2-{3-[3,5-bis(4-{2-ethylhexyloxy}phenyl)phenyl]phenyl}pyridyl)-2-(5-trifluoromethyl-2-*H*-1,2,4-triazolyl)-5-{4-vinylphenyl}pyridyl)]iridium(III) 11

**9** (300 mg, 0.170 mmol) and **10** (11) (51 mg, 0.221 mmol) were dissolved in tetrahydrofuran (2 mL) and aqueous sodium carbonate solution (2 M, 900 μL). The mixture was deoxygenated by two freeze-pump-fill (nitrogen) thaw cycles, and then tetrakis(triphenylphosphine)palladium (0) (21 mg, 18 μmol) was added. The mixture was deoxygenated by two further freeze-pump-fill (nitrogen) thaw cycles and heated at 76 °C for 15 hours in the dark. After cooling diethyl ether (60 mL) and water (60 mL) were added and the layers separated. The organic phase was washed with water (2 × 60 mL), dried over sodium sulfate, filtered and the solvents removed. The residue was purified in two steps; first by column chromatography over silica using diethyl ether:methanol (1:0 → 9:1) mixtures as eluent, and then using light petroleum:ethylacetate (3:1 → 2:1) mixtures as eluent to give **11** (209.4 mg, 69%): (Found: C, 71.37; H, 6.52; N, 4.66. C<sub>106</sub>H<sub>114</sub>F<sub>3</sub>IrN<sub>6</sub>O<sub>4</sub> requires C, 71.3; H, 6.4; N, 4.7%);  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)/nm 273 (log  $\epsilon$ /dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup> 5.23), 361sh (4.22), 397sh (3.77), 421sh (3.67) and 478sh (2.59);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3451, 2957, 2926, 2858, 1608, 1511, 1475, 1249, 1176, 1026 and 826;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.80 – 0.99 (24H, m, Me), 1.27 – 1.60 (32 H, m, CH<sub>2</sub>), 1.76 (4H, m, C<sub>3</sub>CH) 3.90 (8H, m, CH<sub>2</sub>O), 5.20 (1H, d, *J* = 11.0, CCH<sub>2</sub>), 5.59 (1H, d, *J* = 17.7, CCH<sub>2</sub>), 6.40 – 8.40 (44 H, m, ArCHCH<sub>2</sub> and ArH);  $\delta_{\text{C}}$ (125 MHz; CDCl<sub>3</sub>) 11.13, 14.11, 23.07, 23.88, 29.10, 30.54, 39.41, 70.58, 70.60, 114.79, 114.88, 115.38, 119.20, 119.48, 121.35, 121.83, 122.38, 123.29, 123.36, 123.40, 123.46, 123.80, 126.41, 127.17, 128.26, 129.27, 129.83, 132.33, 132.75, 133.41, 133.67, 134.10, 134.90, 135.48, 135.63, 135.89, 137.03, 137.09, 137.49, 138.47, 141.72, 142.02, 142.96, 144.11, 145.30, 147.38, 147.74, 148.49, 149.30, 150.54, 152.41, 159.03, 159.20, 163.49, 167.72, 168.54, 224.13;  $\delta_{\text{F}}$ (377 MHz; CDCl<sub>3</sub>) -63.08 (100%), -63.134 (14); *m/z* (MALDI-TOF) 1785 ([M + H]<sup>+</sup>), 1470 ([M – triazole ligand + H]<sup>+</sup>).

### Poly[4-(bis{2-[3-(3,5-bis{4-[2-ethylhexyloxy]phenyl}phenyl)phenyl]pyridyl}-2-{5-trifluoromethyl-2-*H*-1,2,4-triazolyl}pyrid-5-yl})iridium(III)styrene] 4

**Method 1:** **11** (100 mg, 56.0 μmol) was dissolved in *tert*-butylbenzene (300 μL) and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (14) (17 μg, 0.53 μmol) was added. This mixture was then deoxygenated with three freeze-pump-fill (nitrogen) thaw cycles and heated quickly to 125 °C and then held there for 64 h. After cooling the solution was diluted with dichloromethane (1 mL) and poured into methanol (10 mL) at which time a suspension formed. The suspension was then centrifuged (4500 rpm, 10 minutes) and the solvent decanted. The polymer was then purified by two precipitations as follows: dissolution in dichloromethane (1 mL), precipitation into methanol (10 mL), centrifugation (4500 rpm, 10 minutes) and the solvent decanted. The residue was collected and dried to give **4** (76.5 mg, 77 %): (Found: C, 66.44; H, 6.36; N, 3.85%);  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm 361sh, 426;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3451, 2927, 1609, 1511, 1477, 1250, 1177, 1028, 826;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.40 – 1.00 (24 H, br m, Me), 1.00 – 1.85 (38 H, br m, CH<sub>2</sub> and C<sub>3</sub>CH), 3.50 – 4.08 (8 H, br m, CH<sub>2</sub>O) 6.30 – 8.60 (44 H, br m, ArCHCH<sub>2</sub> and ArH);  $\delta_{\text{C}}$ (125 MHz; CDCl<sub>3</sub>) 11.12, 14.10, 23.06, 23.87, 29.09, 30.54, 39.40, 70.58, 114.79, 114.85, 119.14, 123.79, 128.25, 133.63, 141.74, 159.04, 159.18;  $\delta_{\text{F}}$ (377 MHz, CDCl<sub>3</sub>) -63.08 (100 %), -63.14br (44); *m/z* [MALDI<sup>+</sup>-TOF] 1470;  $\overline{M}_w$  (GPC, THF) 7482, PDI(GPC, THF) 1.77.

*Method 2: 11* (50.0 mg, 28.0  $\mu\text{mol}$ ) was dissolved in a solution of azobis(*iso*-butyronitrile) (46  $\mu\text{g}$ , 0.28  $\mu\text{mol}$ ) in *tert*-butylbenzene (98  $\mu\text{L}$ ). This mixture was deoxygenated with three freeze-pump-fill (nitrogen) thaw cycles and then heated at 140  $^{\circ}\text{C}$  for 16 hours. After cooling the solution was diluted with chloroform (1 mL) and poured into methanol (10 mL) at 0  $^{\circ}\text{C}$ . The supernatant was removed and the residue was purified by size exclusion chromatography (Sephadex LH20) using a dichloromethane:methanol (3:1) mixture as eluent to give **4** (5.7 mg, 12 %):  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  371sh, 433;  $\nu_{\text{max}}/\text{cm}^{-1}$  2927, 1608, 1512, 1477, 1251, 1177, 1029, 826, 731;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  0.40 – 1.05 (24 H, br m, Me), 1.05 – 2.10 (38 H, br m,  $\text{CH}_2$  and  $\text{C}_3\text{CH}$ ), 3.40 – 4.12 (8 H, br m,  $\text{CH}_2\text{O}$ ) 5.80 – 8.60 (44 H, br m, ArCHCH<sub>2</sub> and ArH);  $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$  11.06, 14.07, 23.04, 23.85, 25.71, 27.19, 29.21, 29.68, 30.52, 31.90, 32.80, 39.38, 63.10, 69.71, 70.56, 114.77, 123.76br, 123.38br, 141.70br, 159.02;  $\delta_{\text{F}}(377 \text{ MHz}; \text{CDCl}_3)$  -63.02br;  $m/z$  [MALDI-TOF] 1470;  $\overline{M}_w$  (GPC, THF) 24167, PDI(GPC, THF) 3.59.

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