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A Phosphorescent Poly(dendrimer) Containing Iridium(III) Complexes: Synthesis and Light-Emitting Properties

Wen-Yong Lai,[†,§] Jack W. Levell,[‡] Andrew C. Jackson,[†] Shih-Chun Lo,[*,†]
Paul V. Bernhardt,[†] Ifor D. W. Samuel,[‡] and Paul L. Burn[†]

[†]*Centre for Organic Photonics & Electronics (COPE), The University of Queensland, School of Chemistry and Molecular Biosciences, Chemistry Building, Queensland, 4072 Australia, and* [‡]*Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9SS, U.K.* [§]*Current address: Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing, China, 210046*

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ABSTRACT: A poly(styrene) with pendant dendronized iridium(III) complexes attached to every repeat unit was prepared in good yields using a free radical polymerization of a "macromonomer". The dendronized pendant groups were heteroleptic iridium(III) complexes comprised of two 2-phenylpydridyl ligands, to which first generation biphenyl dendrons with 2-ethylhexyloxy surface groups were attached, and a phenyltriazolyl coligand that formed the attachment point to the polymer backbone. Dendronization of the pendant iridium(III) complexes was found to improve thermal stability, solubility, and solution (61%) and solid-state (13%) photoluminescence quantum yields (PLQYs) relative to the nondendronized homopolymer. Viscosity under normal solution processing conditions of 25 mg/mL was found to be 1.23 cSt. Importantly, although the phosphorescent iridium(III) chromophores are held closely along the polymer backbone, they do not significantly reduce the PLQY in solution by intrachain chromophore interactions. Simple bilayer organic light-emitting diodes comprising a blend of the poly(dendrimer) with 4,4-bis(*N*-carbazolyl)biphenyl and an electron transporting layer had good performance with an external quantum efficiency of 6.2% at 100 cd/m^2.

Introduction

Organic light-emitting diodes (OLEDs) are finding commercial applications in flat-panel displays and solid-state lighting. Tremendous advances have been achieved recently but the development of high-performance materials that are suitable for low-cost large-area fabrication techniques, such as inkjet printing, is still a challenge. Iridium(III)-based phosphorescent materials have given rise to the most efficient OLEDs[1,2] due to the heavy atom effect that allows effective intersystem crossing and harvesting of the singlets and triplets that are formed during device operation. This has led to OLEDs with performances approaching the maximum internal quantum efficiency of 100%.[3,4] Over the past decade, numerous iridium(III)-based phosphorescent materials have been developed with their emission being tuned from saturated blues to reds.[5,6] Most of these structural variations have focused on small molecules that are deposited by high temperature/high vacuum deposition techniques. One method to simplify and lower the cost of device fabrication is to develop solution processable active materials that are suitable for large-area device fabrication. The two strategies reported for improving the solution processability of iridium(III) complexes are incorporation of the iridium(III) complex within a dendritic architecture[7−19] or as part of a polymer structure.[20−34] In the latter case, efforts have focused on random copolymers where only a small number of complexes are attached to or incorporated into the polymer backbone. The reason given for the use of only a small ratio of complex containing monomer in the polymer is to avoid intrapolymer complex interactions that can give rise to self-quenching.The low number of phosphorescent emitters in the polymer structure mimics the strategy used for small molecule systems, in which the emissive complex is dispersed in a host.

Our strategy for developing solution processed iridium(III) complexes has been to incorporate them into a dendritic architecture.[7−13] By using dendrimer generation,[35] the number of dendrons,[9,12] and type of dendrons,[15−19] it is possible to control the intermolecular interactions that affects the luminescence and charge transport of the materials. However, the viscosity of the dendrimer solutions at standard processing concentrations is only slightly greater than the solvent in which they are dissolved.[36] While this works well for simple processing such as spin-coating, it is too low for other solution processing techniques such as inkjet printing. It would, therefore, be ideal if the control over the critical intermolecular interactions afforded by the dendritic architecture could be combined with solutions of higher viscosity.

We have recently reported two poly(styrene) based polymers that have a heteroleptic iridium(III) complex attached to every "monomer" unit.[37,38] Interestingly, it was found that the solution photoluminescence was not completely quenched in spite of the close proximity of the complexes along the polymer chain, although in the solid-state the photoluminescence quantum yield (PLQY) dropped to less than 1%.[37] This has motivated our interest in exploring the development of a new family of phosphorescent materials, namely iridium(III) poly(dendrimers). It was anticipated that introduction of dendrons to encapsulate the iridium(III) complexes on the polymer backbone should reduce the intermolecular interactions that lead to quenching of the luminescence in the solid-state, and that the use of the polymer backbone would improve the solution processability.

In this paper, we present the synthesis of a homopolymer with pendant iridium(III)-cored dendrimers, which we term a

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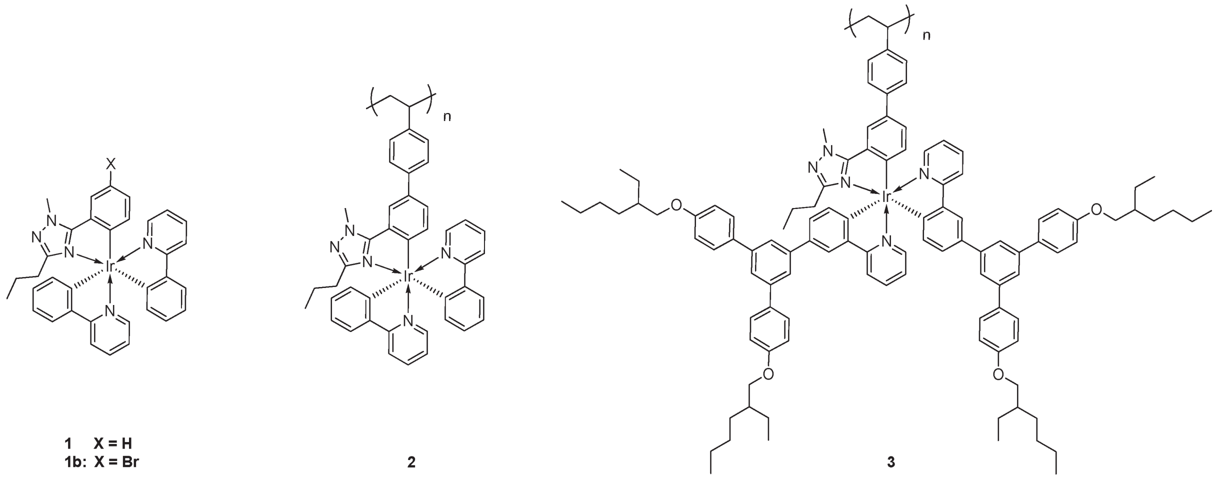
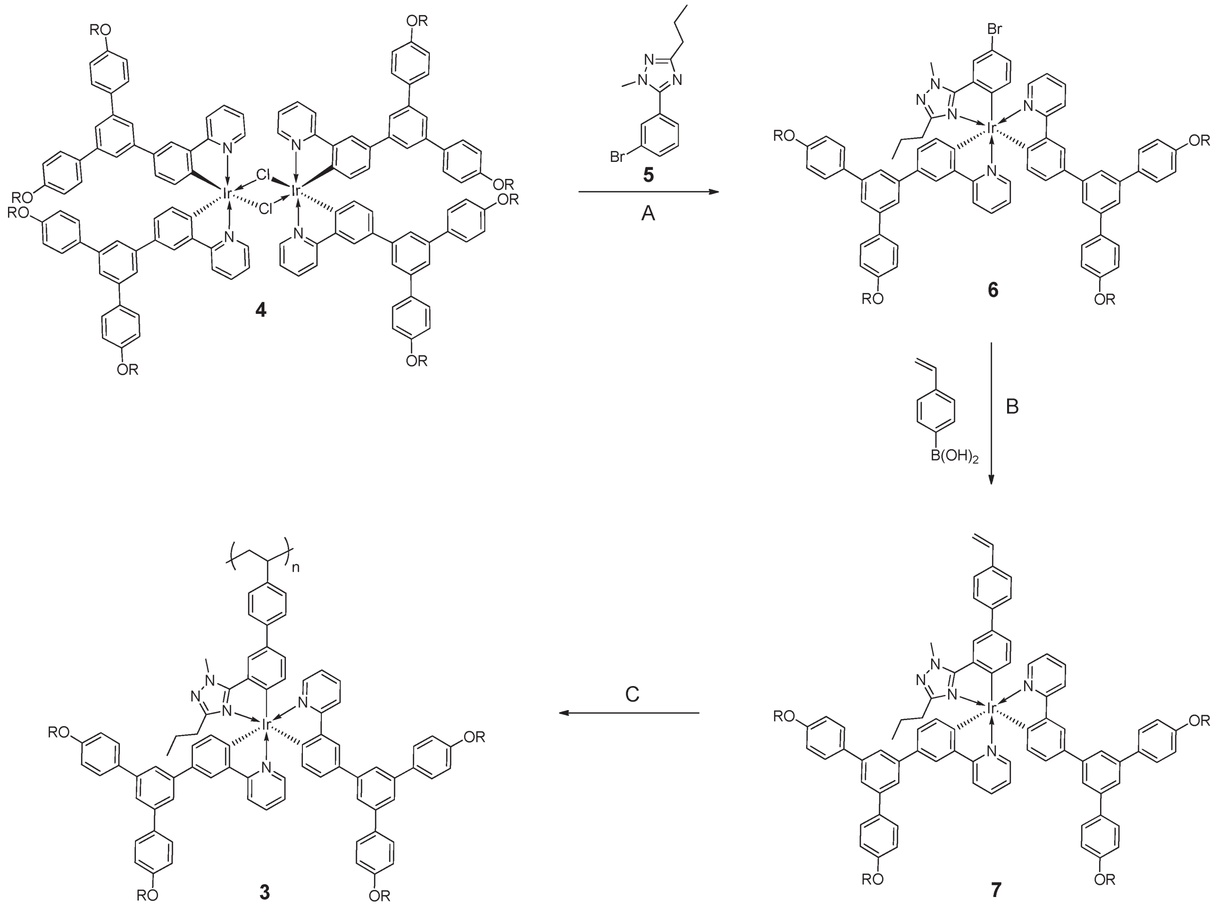
*Corresponding author. E-mail: s.lo@uq.edu.au..



1 X = H
1b: X = Br
2
3

Figure 1. Chemical structures of the target poly(dendrimer) **3**, parent homopolymer counterpart **2**, and model iridium(III) core complexes **1** and **1b**.

Scheme 1[a]

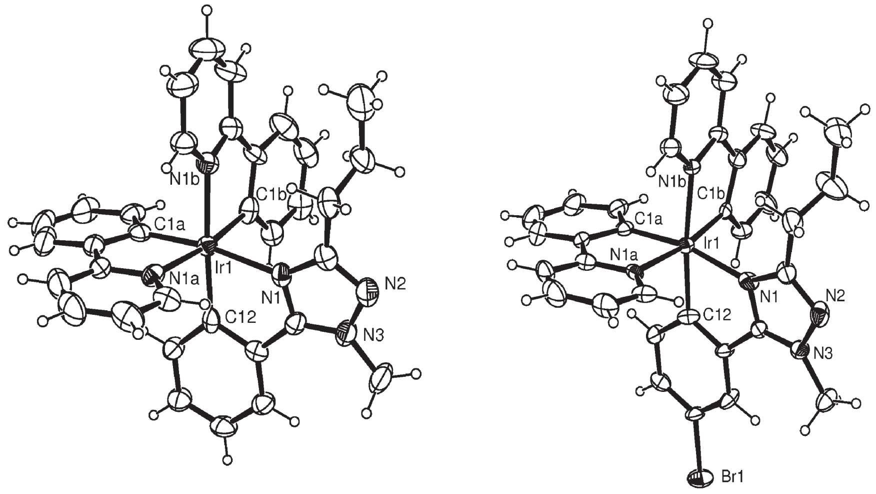


[a] Conditions: (A) silver trifluoromethylsulfonate, heat, Ar; (B) tetrakis(triphenylphosphine)palladium(0), aqueous potassium carbonate, ethanol, toluene, reflux, Ar; (C) 1,1-azobis(cyohexanecarbonitrile), 1-methyl-2-pyrolidinone, heat, Ar (R = 2-ethylhexyl).

"poly(dendrimer)". The poly(dendrimer) has a poly(styrene) backbone with a dendrimer attached to every monomer unit. The dendrimer is comprised of a heteroleptic complex core with two 2-phenylpyridyl ligands and a phenyltriazolyl coligand (**3** in Figure 1). The phenyltriazolyl ligand provides the attachment point to the polymer backbone and first generation biphenyl dendrons with 2-ethylhexyloxy groups are attached to each of the 2-phenylpyridyl ligands. We describe the thermal, electrochemical, photophysical and electroluminescent properties as well as the solubility and viscometric properties of **3**. The chemical structures of **3**, the equivalent nondendronized homopolymer **2**,[38] and the simple complexes **1** and **1b**[38] are shown in Figure 1. Polymer **2** and iridium(III) complexes **1** and **1b** are used for comparative purposes.

Results and Discussion

Synthesis and Characterization. There are three main synthetic approaches that could be used to construct poly(dendrimer) **3**.[39] The first method is a "*graft-onto*" approach,



1 **1b**

Figure 2. X-ray crystal structures of complex **1** and its tris-bromo derivative **1b**.

which is where the whole dendronized complex is connected to the polymer backbone. The second approach is the "*graft-from*" route, whereby the dendrimers are constructed divergently step-by-step from the polymer backbone. However, both these approaches suffer from the problem of incomplete reactions, which results in undesirable structural defects along the polymer backbone. The third approach is the "*macromonomer*", which involves the polymerization of a dendritic macromonomer. The advantage of this latter approach is that every monomer unit within the polymer bears the complete dendrimer. However, the challenge of the macromonomer approach is to achieve higher molecular weights as the bulky dendrimer structure can reduce the efficiency of the polymerization due to steric hindrance.

In our previous work on poly(styrene) homopolymers with small molecule complex side-chains, we found that changing from an acetylacetonoate[37] to a phenyltriazolyl[38] coligand improved the ease of handling and stability of the iridium(III) complex and hence we use the latter coligand in this work. The synthetic route to poly(dendrimer) **3** is shown in Scheme 1. The synthetic procedure for the preparation of the bis-iridium(III) bis-chloro dimer **4** has been reported previously.[7c] Reacting the bis-iridium(III) bis-chloro dimer **4** with 5-(3-bromophenyl)-1-methyl-3-propyl-1*H*-[1,2,4]triazole (**5**)[5c] in the presence of silver trifluoromethanesulfonate at a high reaction temperature of 168 °C without solvent gave dendrimer **6** in a 42% yield. It is known that the cleaving of bis-iridium(III) bis-chloro bridged dimers can lead to either *facial* (the thermodynamically most stable) or *meridional* isomers. However, the determination of the structure of dendrimer **6** by ^{1}H NMR is not straightforward. This is mainly due to the lack of symmetry in **6** and is different from those of the homoleptic tris *facial* isomers such as Ir(ppy)$_3$ that has only one set of ligand signals in ^{1}H NMR due to its C_3 symmetry.[40] To confirm that dendrimer **6** is a thermodynamically stable *facial* isomer, we carried out synthesis of a model complex **1** (Figure 1) and its bromo-derivative **1b**[38] (brominated at the position *para* to the Ir−C bond of the phenyl triazole ligand)[12] under the same reaction conditions. The X-ray crystal structures of **1** and **1b** (Figure 2) clearly showed that they were the *facial* isomers, suggesting that dendrimer **6** is likely to be the *facial* isomer as it was formed under the same complexation conditions.

The styrene moiety to form the macromonomer was introduced via a Suzuki cross-coupling of **6** with 4-vinylphenylboronic acid. The macromonomer **7** was formed in a good yield of 85%. A free-radical polymerization of macromonomer **7** was then carried out using 1,1-azobis(cyclohexanecarbonitrile) as the initiator and 1-methyl-2-pyrolidinone as the solvent. The reaction was heated at 80 °C for 24 h and then poly(dendrimer) **3** was isolated and purified by precipitation from dichloromethane/methanol mixtures to remove the monomer residues and lower molecular weight oligomers. Poly(dendrimer) **3** was isolated in an excellent yield of 86%. Gel permeation chromatography against poly(styrene) standards gave an $\overline{M}_w$ of 2.2×10^4 and an $\overline{M}_n$ of 5.8×10^3 for poly(dendrimer) **3**. Comparison of the $\overline{M}_w$s of **3** and monomer **7** suggests that the poly(dendrimer) **3** consists of around 10 units although a previous report on polydendrimers has shown that gel permeation chromatography can underestimate the molecular weight by a factor of 10.[36]

Poly(dendrimer) **3** was found to be soluble in a range of aprotic solvents including tetrahydrofuran, dichloromethane, chloroform, toluene, 1,2-dichloroethane, and 1-methyl-2-pyrolidinone. In contrast, the nondendronized homopolymer **2** only had good solubility in dichloromethane and 1,2-dichloroethane, showing that the addition of dendrons significantly improves the solubility.[36] One of the key reasons for preparing poly(dendrimer) **3** was to see whether solution viscosity could be increased relative to that of a simple dendrimer. A previous report has shown that at concentrations of up to 25 mg/mL, the viscosity of a dendrimer in solution only increased by 8% relative to that of the solvent.[36]

The viscosity of poly(dendrimer) **3** at various concentrations in 1,2-dichlorobenzene at 20 °C is shown in Figure 3. 1,2-Dichlorobenzene was determined to have a viscosity of 1.06 cSt and at a concentration of 25 mg/mL of poly(dendrimer) **3** in 1,2-dichlorobenzene the viscosity was 1.23 cSt. This is a 16% increase in viscosity, which is double that of a simple dendrimer over the same concentration range.[36] **3** could be spin-coated to form good quality thin films. The films were clear to the eye, indicating there were no large aggregates present and atomic force microscopy (Figure 4) showed that the surface of films spun at 2000 rpm from a 20 mg/mL solution of **3** in dichloromethane had a surface roughness R_a of 0.24 nm, measured over a 10 μm × 10 μm area.

A final aspect of the study of the physical properties of **3** was its thermal properties. While intermediates **6** and **7** were found to have glass transition temperatures (T_g) at 123 and 131 °C (scan rate 200 °C/minute) no glass transition was observed for **3** in range of −20 to +250 °C. The fact that poly(dendrimer) **3** does not have an observable T_g in the

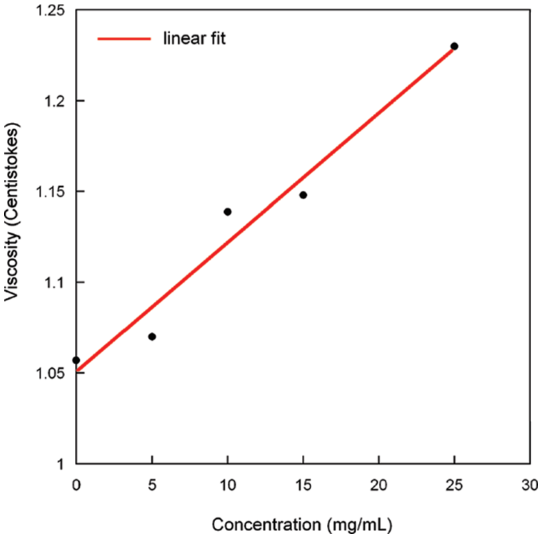


Figure 3. Relationship between viscosity to concentration of poly(dendrimer) **3** in 1,2-dichlorobenzene.

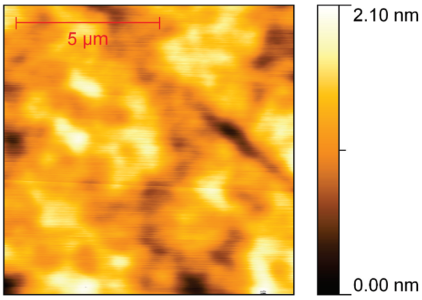


Figure 4. Atomic force microscopy image of a neat film of poly(dendrimer) **3**.

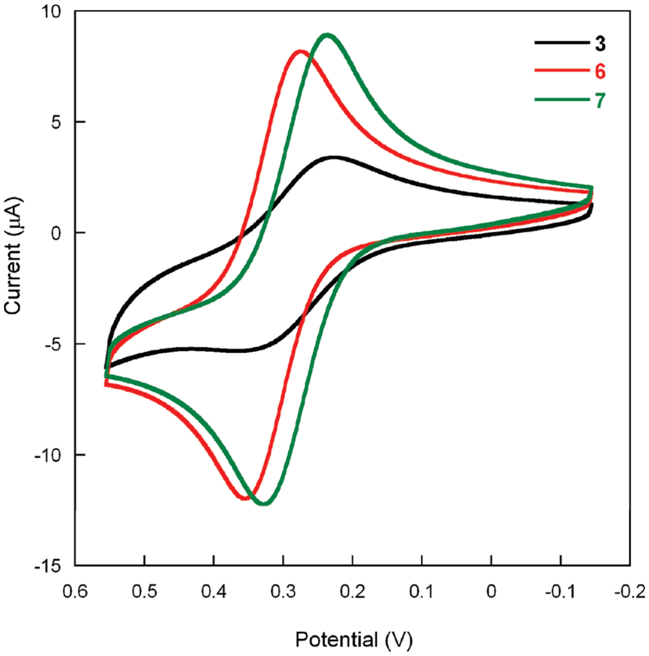


Figure 5. Oxidation cyclic voltammograms of **6**, **7**, and **3** in dichloromethane *versus* the ferrocene/ferrocenium couple (scan rate = 100 mV s^{-1}).

measurement window in contrast to **6** and **7** is due to its higher molecular weight. Thermalgravimetric analysis under nitrogen showed that **3** was stable to thermal degradation with a 5% weight loss only occurring at 410 °C. The degradation temperature for **3** is nearly 40 °C higher than that of the nondendronized homopolymer **2** (371 °C).[38]

Electrochemical Properties. The electrochemical characteristics of the precursor **6**, the monomer **7**, and the poly(dendrimer) **3** were investigated in solution by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell using 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte at room temperature. Figure 5 shows the cyclic voltammograms of **6**, **7**, and **3** in dichloromethane at a scan rate of 100 mV s^{-1}. One chemically reversible oxidation at 0.28, 0.26, and 0.27 V against the ferrocenium/ferrocene couple were obtained for **6**, **7**, and **3**, respectively, which originate from the iridium(III) complex core.[8] The oxidation potentials for **6**, **7**, and **3** are similar to that (0.24 V) reported for a dendrimer with three 2-phenylpyridyl ligands and the same dendrons,[8] indicating that the phenyltriazyloyl coligand is having a minimal effect on the electronic properties of the complexes. In addition, the results show that confining the dendritic iridium(III) complexes on the polymer structure does not change the electronic properties appreciably.

Photophysical Properties. Figure 6a shows the normalized room temperature absorption spectra of precursor **6**, monomer **7**, and poly(dendrimer) **3** measured in dichloromethane. The absorption spectra of these complexes display the usual bands in the UV−visible region. At short wavelengths the strong absorptions are due to the ligand and dendron $\pi-\pi^*$ transitions with the weaker absorptions at longer wavelengths described as the metal-to-ligand charge transfer (MLCT) transitions.[8,41] The similarity of all three spectra indicates that the chromophores of poly(dendrimer) **3** are not interacting strongly even though they are held closely along the polymer chain. Figure 6b compares the normalized absorption spectra of **3** in dichloromethane and the solid-state. The spectra are essentially identical, indicating that there are no strongly aggregating species formed on moving to the solid-state. For some small molecular iridium(III) complex pendant homopolymers, it has been proposed that aggregation can occur during the polymerization due to the close proximity of the iridium(III) complexes.[28] For poly(dendrimer) **3**, the biphenyl dendrons with 2-ethylhexyloxy surface groups attached onto the iridium(III) complexes are likely to act as spacers between the metal complexes on the polymer chain, preventing, at least partially, aggregation.

Photoluminescence Properties. We next investigated the luminescence properties of the materials. Figure 7a shows the normalized photoluminescence (PL) spectra of precursor **6**, monomer **7**, and the poly(dendrimer) **3** in degassed dichloromethane. The emission spectrum of poly(dendrimer) **3** has a peak at 518 nm and a shoulder at 548 nm, which are almost identical to those of the precursor **6** and the monomer **7**. The peak and shoulder are also essentially at the same positions as the dendrimer with three 2-phenylpyridyl ligands and the same dendrons.[8] The fact that the emissions of **3**, **6**, and **7** are similar is important as the homoleptic complex with three phenyltriazolyl ligands emits blue light.[5c] This means that in the heteroleptic complexes of this work the lowest energy emissive transitions are associated with the 2-phenylpyridyl ligands and the phenyltriazolyl ligand is not having a strong effect. In the solid-state [either as a neat film or a 20 wt % blend with 4,4′-bis(*N*-carbazolyl)biphenyl (CBP)], only a very slight red-shift (3−5 nm) in the emission maxima was observed for poly(dendrimer) **3** with respect to that in dilute solution (Figure 7b). The similarity between the solution and film photoluminescence spectra indicates that there are not strong inter- or intrapolymer chromophore interactions that lead to aggregation or excimer formation in the solid-state. The dendritic architecture of

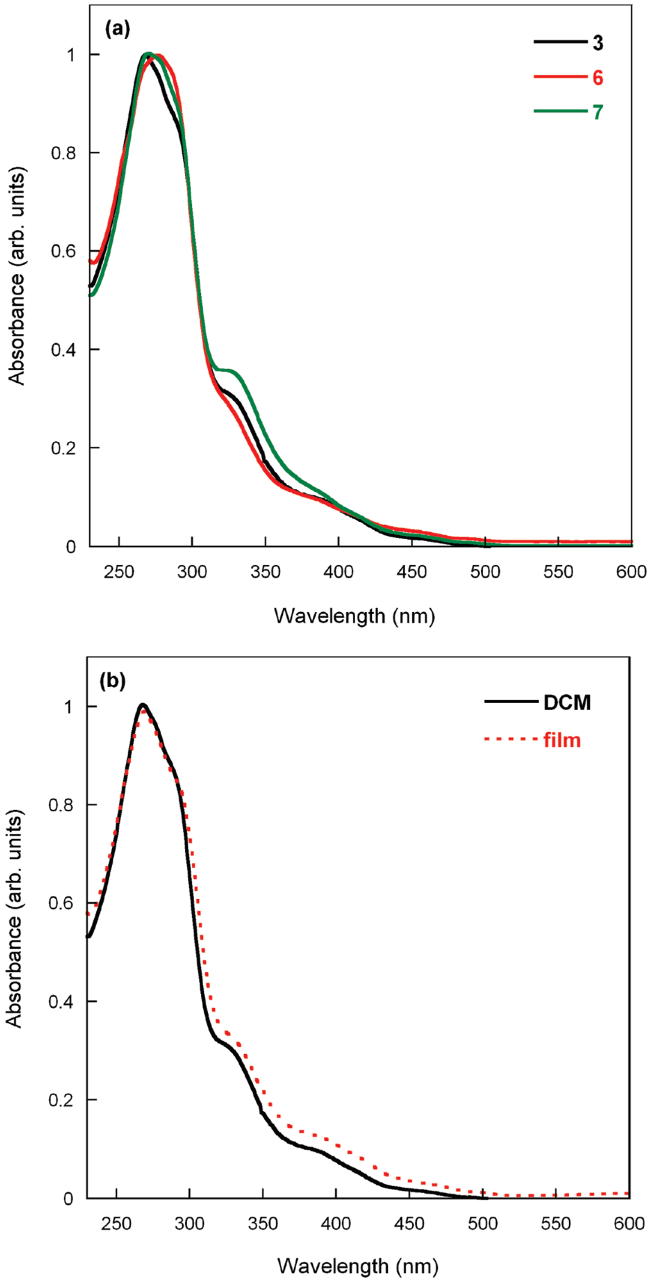


Figure 6. (a) Normalized UV−visible solution absorption spectra of the precursor **6**, the monomer **7**, and the poly(dendrimer) **3** in dichloromethane. (b) Comparison of solution (in dichloromethane) and film UV−visible absorption of poly(dendrimer) **3**.

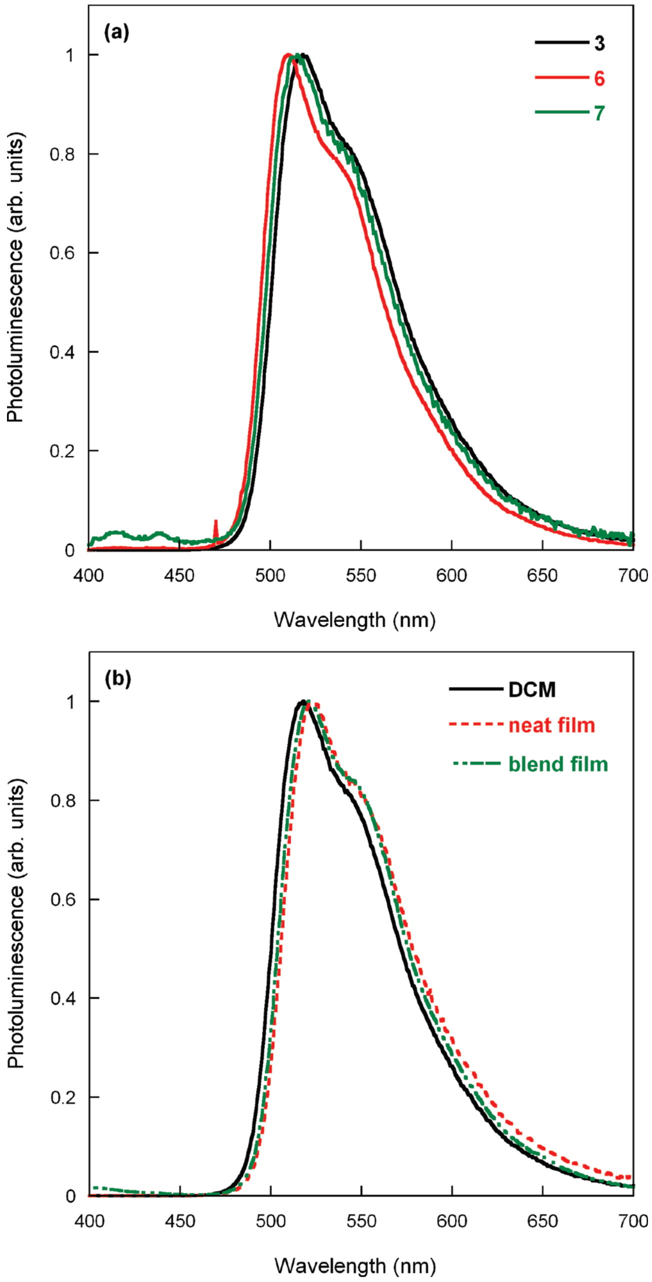


Figure 7. (a) Normalized PL spectra of **6**, **7**, and poly(dendrimer) **3** in degassed dichloromethane; (b) Comparison of PL spectra of poly(dendrimer) **3** in dilute dichloromethane, neat film, and blend film with 20 wt % of **3** in CBP (excitation wavelength = 360 and 325 nm for solution and film, respectively).

poly(dendrimer) **3** controls to a first approximation detrimental interchromophore interactions.

Solution PLQYs of **3**, **6**, and **7** were found to be 61%, 92%, and 7%, respectively. The precursor **6** emits bright green light and the photoluminescence shows a monoexponential decay with a lifetime of 1.6 μs. It is interesting to note that the attachment of the styrene unit required for the polymerization caused a dramatic decrease in the PLQY of complex **7** (7%) and the photoluminescence decay was biexponential with a large (66% pre-exponential factor) fast component (0.18 μs) and a smaller (34%) slower (0.94 μs) component. The biexponential decay indicates that there is more than one emissive species present in the complex. The shorter lifetime and lower PLQY of complex **7** when compared to **6** clearly shows that the presence of the styrene group leads to an additional efficient nonradiative pathway in the monomer complex **7**. Importantly, the polymerization of the dendritic monomer **7** to form **3** results in a saturated polymer backbone and **3** has an excellent PLQY of 61%. The decay of the photoluminescence is again biexponential decay but in this case both components are of order microseconds [1.03 μs (58%) and 1.95 μs (42%)], which is consistent with the much higher PLQY. Given the effect of the vinyl moiety on the PLQY it is important that no unsaturation is left in the polymer backbone. The PLQY of **3** is over twice that of the nondendronized polymer **2**, which had a PLQY of 23%,[38] and this again demonstrates the positive effect of dendronization. The high solution PLQY of **3** is also indicative of there not being strong intrachain chromophore interactions that lead to substantial photoluminescence quenching.

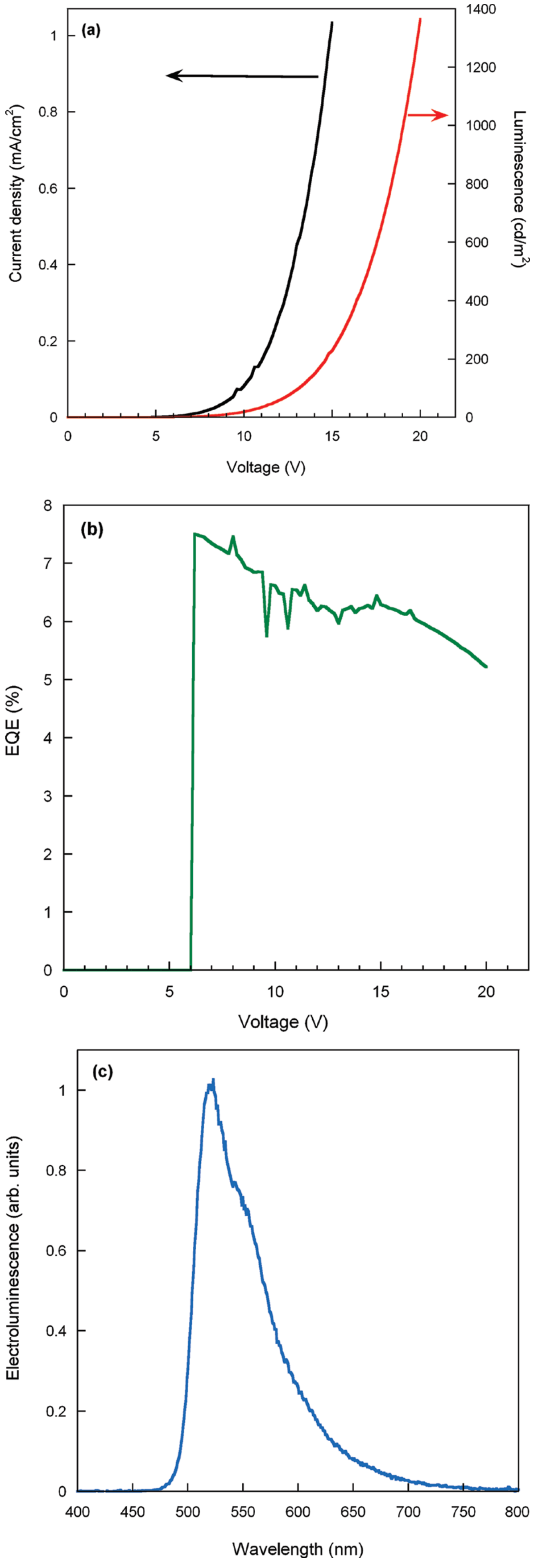


Figure 8. OLED characteristics of poly(dendrimer) **3** with the device configuration of ITO/**3**:CBP (20 wt %)/TPBI/LiF/Al: (a) current density−voltage−brightness characteristics; (b) EQE (external quantum efficiency)−voltage characteristics; (c) EL spectrum.

The neat film PLQY of **3** was measured to be 13%. This is a significant improvement on the solid-state PLQY of a nondendronized iridium(III) complex containing homopolymer, which had a film PLQY of less than 1%.[37] The fact that the solid-state PLQY of **3** is less than that in solution indicates that there are interchromophore interactions (either intra- or inter-chain) that have not been completely controlled. Nevertheless it is still a significant step forward in materials design. The good solubility of **3** enabled it be blended with CBP. At a 20 wt % blend film, the film PLQY increased to 42%, indicating that interchain interactions were playing a role in photoluminescence quenching in the neat films.

Electroluminescent Properties. OLEDs with a configuration of ITO/**3**:CBP (20 wt %)/TPBI/LiF/Al were manufactured and the device properties are summarized in Figure 8. 1,3,5-Tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) was used as the hole blocking/electron transporting layer to balance electron and hole currents.[7a] The device had a luminance of 1364 cd/m^2 at 20 V. The electroluminescence had a peak at 520 nm (Figure 8) and the emission color was a saturated green with CIE 1931 coordinates of (0.34, 0.62). The maximum external quantum efficiency (EQE) of 7.5% (26.4 cd/A) was achieved at 6.2 V and it remained as high as 6.2% (21.8 cd/A) at 100 cd/m^2 (13.1 V), and 5.5% (19.3 cd/A) at 1,000 cd/m^2 (19 V). An external quantum efficiency of 6% is close to the maximum possible of 8% based on the PLQY (42%) of the blended film and assuming 20% light outcoupling efficiency. This implies that the charge balance is good in these devices but the relatively high drive voltages implies that the charge transport in the poly(dendrimer)−CBP blend needs to be improved.

Conclusion

A phosphorescent polymer with a polystyrene backbone and pendant dendritic iridium(III) complexes attached to every repeat unit has been prepared. The use of a phenyltriazolyl coligand gave rise to a stable heteroleptic complex, which could be easily elaborated to form a macromonomer. The "macromonomer" approach to the polymer using a free-radical polymerization resulted in a good yield. The use of dendronized iridium(III) complexes improved the solubility and photoluminescence (both in solution and the solid-state) relative to nondendronized polymers illustrating the power of dendronization. Poly(dendrimer) **3** also exhibited a higher viscosity than that of a simple dendrimer analogue, showing the way forward for the development of materials for inkjet printing. While the solution PLQY of poly(dendrimer) **3** was good, in the solid-state there were still interactions that led to a decrease in the PLQY. Changing the generation and/or number of dendrons could be used to overcome this problem. Finally, we have demonstrated that simple efficient OLEDs can be manufactured using poly(dendrimers).

Experimental Section

Measurements. All commercial reagents were used as received unless otherwise noted. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere before use. ^{1}H and ^{13}C NMR spectra were recorded using a 300 or 400 MHz Bruker spectrometer, in deuterated chloroform solution; EH = 2-ethylhexyl, Pr = *n*-propyl, BP H = branch phenyl H, L H = ligand phenyl/pyridyl H, SP H = surface phenyl H, styrylP H = protons of the phenyl ring attached to the vinyl moiety, EtP H = protons of the phenyl ring attached to the ethyl moiety. All coupling constants (J) are in Hertz and quoted to the nearest 0.5 Hz. Gel permeation chromatography (GPC) was carried out on a Waters GPC system, consisting of a 1515 Isocratic pump (Waters), a 717 autosampler (Waters), and Styragel HT3 and HT6E columns (300 mm +300 mm lengths, 7.8 mm diameter), calibrated with polystyrene (Waters) narrow standards ($\bar{M}_p = 1.06 \times 10^3$ to 1.32×10^6) in tetrahydrofuran with toluene as flow marker at the Australian National Fabrication Facility (Queensland Node). The tetrahydrofuran was pumped at a rate of 1 cm^3/min at 40.0 °C. Microanalyses were carried out at the Microanalysis Laboratory, School of Chemistry and Molecular Biosciences, The University of Queensland. UV−visible absorption measurements were recorded with a Cary Varian 5000 UV−vis−NIR spectrophotometer. Melting points were measured in a glass capillary on a BÜCHI Melting Point B-545 and are uncorrected. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer STA6000 and differential scanning calorimetry was performed using a Perkin-Elmer Diamond DSC. 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 using a homemade OSTWALD viscometer at a constant temperature of 20 °C. Deionized freshly distilled water with viscosity of 1.00 cSt at 20 °C has been used as a reference.[42]

Electrochemistry was performed using a BAS Epsilon electrochemistry station using a glassy carbon working, 0.1 M $AgNO_3$ in acetonitrile reference, and platinum counter electrode. All measurements were carried out at room temperature with samples at a 1 mM concentration in dichloromethane (HPLC grade), and 0.1 M tetra-*n*-butylammonium tetrafluoroborate as electrolyte. The solutions were deoxygenated with argon and the ferricenium/ferrocene couple was used as standard.[43] 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.

AFM measurements were made using a Veeco Caliber AFM operating in contact mode. The scans were made at a scan rate of one line per second and a resolution of 1024 × 1024 points was used for a 10 μm × 10 μm area.

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.[44] 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 (less than/equal to 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 Picoquanct GaN laser diode and an instrument response of ~1 ns. For solid-state PLQY measurements, the sample was placed in an integrating sphere under a nitrogen purge and excited with the 325 nm line of a He−Cd laser at a power of ~0.3 mW. The luminescence was detected from a calibrated photodiode behind a UV filter and the PLQY was calculated in accordance with the method of Greenham et al.[45]

OLEDs were fabricated on ITO substrates that were etched using zinc powder and HCl. The substrates were cleaned by sonication in acetone and then 2-propanol before oxygen plasma ashing. The blend film was spin-coated from a 20 mg/mL solution of **3**:CBP (20 wt %) in DCM at 2000 rpm. The devices were then placed in an evaporator operating at a pressure of 10^{-6} mbar and a 60 nm hole blocking, 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) layer, followed by sequential deposition of a 0.7 nm thin layer of LiF and > 100 nm aluminum cathode were deposited by thermal vapor deposition.

Synthesis of model complex 1. A mixture of the bis-iridium bischloro dimer (200 mg, 0.187 mmol), 1-methyl-3-propyl-5-phenyl-1*H*-[1,2,4]triazole[5c] (402 mg, 1.87 mmol), and silver trifluoromethanesulfonate (169 mg, 0.659 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 the residue was purified by column chromatography over silica using dichloromethane/light petroleum (2:1) as eluent to give **1** as a bright yellow powder (76.5 mg, 29%); mp > 322.5 °C (dec). Anal. Calcd for $C_{34}H_{30}IrN_5$: C, 58.3; H, 4.3; N, 10.0. Found: C, 58.1; H, 4.4; N, 9.8. ^{1}H NMR (300 MHz; $CDCl_3$): δ 0.55 (3H, t, *J* = 7.5, Pr CH_3), 1.18−1.42 (2H, m, Pr CH_2), 1.78−1.92 (2H, m, Pr CH_2), 4.18 (3H, s, NCH_3), 6.70−7.00 (11H, m, L H), 7.48−7.68 (6H, m, L H), and 7.82−7.93 (3H, m, L H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 13.8, 21.7, 28.7, 37.8, 118.3, 118.8, 119.68, 119.74, 119.8, 121.3, 121.9, 123.7, 123.8, 123.9, 129.7, 129.8, 129.9, 132.1, 135.7, 135.9, 136.3, 136.6, 138.4, 143.5, 144.0, 147.7, 147.8, 159.9, 160.7, 160.9, 161.1, 163.4, 166.5, 167.2. *m*/*z* (MALDI: DCTB): calcd for $C_{42}H_{36}IrN_5$, 699.2 (57%), 700.2 (22%), 701.2 (100%), 702.2 (39%), 703.2 (8%); found, 699.2 (61%), 700.2 (28%), 701.2 (100%), 702.2 (33%), 703.2 (6%). Excess ligand 1-methyl-3-propyl-5-phenyl-1*H*-[1,2,4]triazole (260 mg) was recovered, which co-chromatographed with and had an identical ^{1}H NMR as an authentic sample.

Synthesis of **6**. A mixture of **4**[7c] (400 mg, 0.133 mmol), **5**[5c] (372 mg, 1.33 mmol), and silver trifluoromethanesulfonate (131 mg, 0.51 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 **6** as a bright yellow powder (194.5 mg, 42%); T_g 129 °C; TGA$_{(5\%)}$ 383 °C. Anal. Calcd for $C_{102}H_{117}BrIrN_5O_4$: C 70.0, H 6.7, N 4.0. Found: C 69.7, H 6.8, N 4.0. λ_{max} (CH_2Cl_2)/nm: 276 (log ε/dm^3 mol^{-1} cm^{-1} 5.30), 326 sh (4.76), 384 sh (4.19), 409 sh (4.00), 456 sh (3.54), and 489 sh (3.02). ^{1}H NMR (400 MHz; $CDCl_3$): δ 0.66 (3H, t, *J* = 7, Pr CH_3), 1.00−1.12 (24H, m, EH CH_3), 1.40−1.75 (34H, m, EH CH_2, and Pr CH_2), 1.84−2.02 (6H, m, EH CH, and Pr CH_2), 3.94−4.07 (8H, m, $ArOCH_2$), 4.21 (3H, s, NCH_3), 6.87 (1H, t, *J* = 6.5, L H), 6.98 (1H, d, *J* = 8, L H), 7.04−7.16 (12H, m, SP H, and L H), 7.33 (1H, m, L H), 7.41 (1H, m, L H), 7.56 (1H, m, L H), 7.66 (1H, m, L H), 7.69−7.83 (12H, m, SP H, BP H, and LH), 7.85 (2H, d, *J* = 1.5, BP H), 7.91 (2H, d, *J* = 1.5, BP H), 7.95 (1H, d, *J* = 5, L H), 8.01 (1H, d, *J* = 8.5, L H), 8.06 (1H, d, *J* = 8.5, L H), 8.08 (1H, s, L H), and 8.11 (1H, s, L H). ^{13}C NMR (100 MHz; $CDCl_3$): δ 11.3, 13.9, 14.2, 21.8, 23.2, 24.0, 27.0, 28.8, 29.2, 30.7, 37.9, 39.6, 70.7, 113.7, 114.9, 118.7, 119.2, 121.8, 122.3, 122.8, 123.3, 123.6, 123.7, 126.5, 128.3, 128.4, 129.2, 129.3, 132.6, 133.27, 133.30, 133.8, 133.9, 134.4, 136.2, 136.4, 136.9, 137.1, 140.3, 141.84, 141.88, 143.3, 143.5, 144.3, 144.8, 147.7, 148.0, 159.1, 159.1, 160.1, 161.3, 162.2, 166.2, 167.0; *m*/*z* [MALDI: DCTB]: calcd for $C_{102}H_{117}BrIrN_5O_4$, 1745.8 (28%), 1746.8 (33%), 1747.8 (95%), 1748.8 (96%), 1749.8 (100%), 1750.8 (75%), 1751.8 (38%), 1752.8 (14%), 1753.8 (4%), found, 1745.8 (28%), 1746.8 (31%), 1747.8 (100%), 1748.8 (90%), 1749.8 (99%), 1750.8 (67%), 1751.8 (38%), 1752.8 (14%), 1753.8 (3%). GPC: $\bar{M}_w = 1876$, $\bar{M}_v = 1875$, PD = 1.00. Excess ligand **5** (288 mg) was recovered, which cochromatographed with and had an identical ^{1}H NMR as an authentic sample.

Synthesis of **7**. A mixture of **6** (100 mg, 0.057 mmol), 4-vinylphenylboronic acid (21.2 mg, 0.143 mmol), tetrakis(triphenylphosphine)palladium(0) (6.6 mg), aqueous potassium carbonate (2 M, 0.4 mL), ethanol (0.4 mL), and toluene (1.1 mL) was deoxygenated (by placing under vacuum and backfilling with argon) and then heated at reflux under argon for 24 h. The mixture was allowed to cool to room temperature and then water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic portions were combined and washed with brine (12 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane/light petroleum mixtures (1:1) as eluent to give **7** as a bright yellow powder (86.4 mg, 85%); mp 154−182 °C; TGA$_{(5\%)}$ 395 °C. Anal. Calcd for $C_{110}H_{124}IrN_5O_4$: C, 74.5; H, 7.1; N, 4.0. Found: C, 74.3; H, 7.2; N, 3.9. ν_{max}(solid)/cm^{-1}: 677.5, 707.5, 729.5, 747.7, 782.7, 824.0, 872.3, 1027.0, 1063.8, 1110.8, 1175.9, 1235.0, 1281.0, 1422.2, 1473.7, 1508.6, 1595.4, 2857.5, 2924.6, 2955.9. λ_{max}(CH_2Cl_2)/nm: 270 (log ε/dm^3 mol^{-1} cm^{-1} 5.25), 326 sh (4.78), 384 sh (4.15), 409 sh (3.92), 456 sh (3.38), and 491 sh (2.96). ^{1}H (300 MHz; CDCl$_3$): δ 0.63 (3H, t, J = 7.5, Pr CH$_3$), 0.92−1.08 (24H, m, EH CH$_3$), 1.31−1.69 (34H, m, EH CH$_2$, and Pr CH$_2$), 1.75−2.03 (6H, m, EH CH, and Pr CH$_2$), 3.88−4.03 (8H, m, ArOCH$_2$), 4.31 (3H, s, NCH$_3$), 5.28 (1H, d, J = 11, Vinyl H), 5.81 (1H, d, J = 17.5, Vinyl H), 6.78 (1H, dd, J = 11, and 17.5, Vinyl H), 6.88 (1H, t, J = 7, L H), 6.98−7.12 (13H, m, SP H, and LH), 7.19 (1H, dd, J = 2, and 8, L H), 7.28−7.38 (2H, m, L H), 7.49 (2H, m, 1/2AA′XX′, styrylP H), 7.56−7.77 (17H, m, 1/2AA′XX′, styrylP H, BP H, SP H, and L H), 7.78−7.88 (4H, m, BP H), 7.96−8.01 (5H, m, L H). ^{13}C NMR (75 MHz; CDCl$_3$): δ 11.2, 13.9, 14.1, 21.7, 23.1, 23.9, 28.8, 29.1, 30.6, 38.0, 39.5, 70.6, 113.2, 114.8, 118.7, 119.1, 121.7, 122.1, 122.2, 122.7, 123.2, 123.56, 123.63, 126.4, 126.7, 128.28, 128.32, 128.6, 129.1, 129.2, 132.4, 133.0, 133.8, 133.9, 135.6, 136.0, 136.3, 136.6, 136.8, 137.1, 138.8, 141.4, 141.7, 141.8, 143.3, 143.5, 144.3, 144.7, 147.8, 148.0, 159.1, 159.5, 160.4, 160.5, 161.2, 163.3, 166.4, 167.1; m/z (MALDI: DCTB): calcd for $C_{110}H_{124}IrN_5O_4$, 1769.9 (41%), 1770.9 (51%), 1771.9 (100%), 1772.9 (99%), 1773.9 (58%), 1774.9 (23%), 1775.9 (7%), 1776.9 (2%); found, 1769.9 (50%), 1770.9 (52%), 1771.9 (100%), 1772.9 (99%), 1773.9 (64%), 1774.9 (38%), 1775.9 (15%), 1776.9 (6%). GPC: $\overline{m}_w$ = 1976, $\overline{m}_v$ = 1974, PD = 1.00.

Synthesis of Poly(dendrimer) ***3***. 1,1-Azobis(cyclohexanecarbonitrile) (5.3 mg) was dissolved in 1-methyl-2-pyrolidinone (0.6 mL). 120 μL of the above solution was added into a Schlenk tube that was charged with **7** (130 mg, 0.073 mmol). 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. Dichloromethane (3 mL) was added to the reaction mixture, which was then poured into a stirred methanol (20 mL). The precipitate was collected at the filter. The reprecipitation procedure was repeated twice more to remove the monomer residues and low-mass counterparts. The precipitate was collected and dried to give **3** as a bright yellow powder (112 mg, 86%); mp 249−268 °C; TGA$_{(5\%)}$ 410 °C. Anal. Calcd for $(C_{110}H_{124}IrN_5O_4)_n$: C, 74.5; H, 7.1; N, 4.0. Found: C, 74.4; H, 7.1; N, 4.1. λ_{max}(CH$_2$Cl$_2$)/nm: 268, 290 sh, 326 sh, 384 sh, 409 sh, 460 sh, and 496 sh. ^{1}H (400 MHz; CDCl$_3$): δ 0.61−0.63 (br, Pr CH$_3$), 0.78−1.01 (br, CH$_2$ and/or Pr CH$_2$), 1.23−1.91 (br, CH$_2$ and/or Pr CH$_2$ and CH), 3.59−3.94 (br, CH$_2$), 4.12−4.37 (brm, NCH$_3$), 6.62−7.17 (brm, SP H, BP H, styrylP H and/or LH), 7.39−8.15 (brm, SP H, BP H, EtP H and/or LH). GPC: $\overline{M}_w$ = 2.2×10^4, $\overline{M}_n$ = 5.8×10^3, PD = 3.78.

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Supporting Information Available: Figures showing ORTEP diagrams of **1** and **1b** and tables of crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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