Synthesis and Properties of Highly Efficient Electroluminescent Green Phosphorescent Iridium Cored Dendrimers

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ABSTRACT: A simple convergent procedure has been developed for the preparation of solution processable phosphorescent dendrimers with biphenyl-based dendrons and *fac*-tris(2-phenylpyridyl)iridium(III) cores. We found that the attachment point and branching of the dendrons are important for controlling the color of the light emission. Photoluminescence excitation measurements showed that energy could be transferred efficiently from the dendrons to the core. Solution photoluminescence quantum yield (PLQY) measurements of the dendrimers were of order 70%, showing that the attachment of the dendron did not decrease the luminescence efficiency of the core iridium complex. The PLQYs of the neat dendrimer films increased with generation with the second-generation dendrimer having a neat film PLQY of 31%, $1^{1/2}$ times higher than the first-generation dendrimers and almost 3 times that of the nondendritic iridium complex, demonstrating the power of the dendrimer architecture to control intermolecular interactions. Electrochemical experiments showed that charge was injected directly into the core of the dendrimers.

Introduction

One of the revolutions in organic conjugated materials was the discovery that those, which were luminescent in the solid state, could be used as the light-emitting layer in organic light-emitting diodes (OLEDs). The first materials used in OLEDs were fluorescent small molecules, and these materials are processed by evaporation.¹ The discovery that conjugated polymers could be used as the light-emitting element in OLEDs introduced the idea that solution processing could also be used for making large-area OLEDs.² More recently, dendritic macromolecules have been developed as an alternative class of materials for solution-processed light emitters.³⁻⁵ Light-emitting dendrimers consist of surface groups, dendrons, and cores with the latter usually being the emissive chromophore. Although conjugated polymers have made excellent progress, dendrimers have a number of potential advantages for OLEDs formed by solution processing. First, the electronic and processing properties can be optimized independently. Second, a convergent synthesis allows a modular approach to their preparation, meaning that different dendrimer structures can be formed in a simple manner from common dendron intermediates.⁶ Third, the dendrimer generation can be used to control the intermolecular interactions, which are key to governing OLED performance.7 Finally, phosphorescent dendrimers can be easily accessed.^{8–11} The advantage of phosphorescent emitters is that they give the opportunity to provide OLEDs with internal efficiencies of 100% due to their ability to harness both singlet and triplet excited states. In contrast, fluorescent emitters tend to suffer from a substantial loss of efficiency due to triplet formation.¹² The main molecular phosphorescent materials studied have been based on iridium(III) complexes.¹³ The iridium complexes have been used to form highly efficient OLEDs, and their success has been due to their relatively short triplet lifetime and the ability to modify their structure to tune the color of emission.¹³ In common with fluorescent small molecules most studies on phosphorescent emitters have concentrated on molecular materials which are also processed by evaporation. More recently, there has been more effort on developing solution-processed phosphorescent materials.^{8–11,14} Of these routes we have demonstrated that solution processed phosphorescent dendrimers can give very efficient single and bilayer OLEDs.^{9–11,15}

The phosphorescent dendrimers used as the lightemitting component in these highly efficient OLEDs have all been comprised of 2-ethylhexyloxy surface groups, biphenyl-based dendrons, and *fac*-tris(2-phenylpyridyl)iridium(III) (Irppy₃) cores. In our previous reports on these materials we have compared the effect of generation,¹⁰ attachment point of the dendron,¹¹ and device architecture^{9,15} on OLED performance. In this paper we describe the syntheses of these highly efficient dendrimers and illustrate the modularity of the approach. We also discuss the effect of dendrimer generation and dendron attachment point on the physical, photophysical, and electrochemical properties of the dendrimers with the molecular Irppy₃.

Results and Discussion

Synthesis. The properties of dendrimers can be affected by the position of attachment of the dendron to the core as well as the generation of the dendrimer. In this new field of phosphorescent dendrimers **12** and **14** (Scheme 2) to explore the effect of the dendron attachment position on the properties of the core Irppy₃ complex. Dendrimers **12** and **14** differ in that the dendron in **12** is attached *meta* to the pyridyl moiety on the ligand phenyl ring whereas for **14** the dendron is *para* to the pyridyl ring. These different positions have been denoted as 3-G1-IrppyD for **12** and 4-G1-IrppyD for **14** in Scheme 2. We have also studied the

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Scheme 1^a



^{*a*} Key: (A) *tert*-Butyllithium, tetrahydrofuran, dry ice/acetone bath, Ar then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and rt; (B) tetrakis(triphenylphosphine)palladium(0), aqueous sodium carbonate, ethanol, toluene, reflux, Ar.

second-generation dendrimer **13**, which has the same attachment point as **12** and is denoted 3-G2-IrppyD (Scheme 2), to elucidate the effect of dendrimer generation on the properties of the core. There are a number

of elegant routes to biphenyl-based dendrons and dendrimers.¹⁶ We chose a convergent strategy for the formation of the dendrimers with the steps shown in Schemes 1 and 2. The basic synthetic strategy was to



^{*a*} Key: (A) Iridium(III) chloride trihydrate, water, 2-ethoxyethanol, heat then **6**, **8**, or **11**, silver trifluoromethanesulfonate, heat, Ar.

attach the dendrons to the 2-phenylpyridyl ligand and then complex the "dendronized" ligands to the iridium-(III) cation. 2-Ethylhexyloxy groups were chosen as the surface groups for the dendrimers as they have been successfully used for the formation of spin-coated thin films of conjugated polymers.¹⁷ The key intermediate in the synthesis of all the dendrimers was the firstgeneration boronate ester [G1-B(OCMe₂)₂], 4 (Scheme 1). **4** is a first-generation dendron as there is one level of branching from the phenyl group attached to the boronate ester. 4 was formed in three steps from 1-bromo-4-(2'-ethylhexyloxy)benzene (1).18 The first step was the formation of the "zeroth"-generation boronate ester $[G0-B(OCMe_2)_2]$ (2) from 1, which was achieved in a 69% yield by metalation of **1** with *tert*-butyllithium at low temperature followed by reaction with the 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPT-DB). The first-generation bromo-focused dendron (G1-Br) **3** was then formed by reaction of 2.2 equiv of **2** with 1,3,5-tribromobenzene, using palladium catalysis, in a 60% yield. In addition to the desired 3, the trisubstituted

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product, 1,3,5-tris[4'-(2"-ethylhexyloxy)phenyl]benzene, was also isolated in a 27% yield. **3** was then transformed into the first-generation boronate ester **4** in a 75% yield by metalation at low temperature and reaction with IPTDB. To complete the syntheses of the first-generation ligands **6** (3-G1-Lig) and **8** (4-G1-Lig), **4** was coupled with 2-(3'-bromophenyl)pyridine (**5**)¹⁹ and 2-(4'-bromophenyl)pyridine (**7**)²⁰ using tetrakis(triphenylphosphine)palladium(0) in an ethanol/toluene mixture heated at reflux. Under these conditions **6** and **8** were formed in 99% and quantitative yields, respectively.

The strategy for making the second-generation ligand 11 (3-G2-Lig) was slightly different (Scheme 1). The normal method to form the second-generation "dendronized" ligand would be to couple 2 equiv of 4 with 1,3,5-tribromobenzene followed by boronate ester formation and subsequent palladium-catalyzed coupling to 2-(3'-bromophenyl)pyridine (5). Although this route is feasible, we found that the procedure illustrated in Scheme 1 was more efficient. The first step in the alternative procedure was to form the boronate ester of 2-(3'-bromophenyl)pyridine (5). The boronate ester $[Lig-B(OCMe_2)_2]$ (9) was formed by metalation of 5 with tert-butyllithium at low temperature followed by reaction with IPTDB with 9 being isolated in a 50% yield. 9 was then coupled with 1.2 equiv of 1,3,5-tribromobenzene under palladium catalysis to give the dibromophenyl derivative 10 (Lig-DiBrPh) in a 66% yield. The final step in the formation of the second-generation ligand was the coupling of 2.8 equiv of the first-generation dendron 4 with 10. Using the same palladium catalysis conditions as in the earlier steps, the second-generation ligand 11 (3-G2-Lig) was formed in a 98% yield. Therefore, the sequence used for making the dendrons required only two reaction types: the formation of borate esters and their subsequent palladium-catalyzed coupling with aryl bromides.

The iridium complexes were then formed from iridium chloride trihydrate using the same two-step procedure used for molecular iridium complexes (Scheme 2).²¹ The first step for the dendritic complexes involved heating iridium chloride trihydrate with an excess of the requisite dendritic ligand in aqueous 2-ethoxyethanol. Although we could isolate the corresponding intermediate iridium dimers, we found it simpler to just collect the excess ligand from the initial reaction and react it with the crude iridium dimer using silver trifluoromethylsulfonate to drive the reaction forward. This second step was carried out in the melt at temperatures in the region of 130-145 °C depending on the dendrimer. Using this protocol, the first-generation dendrimers 12 (with the dendron in the 3-position; 3-G1-IrppyD) and 14 (with the dendron in the 4-position; 4-G1-IrppyD) and second-generation dendrimer 13 (with the dendron in the 3-position; 3-G2-IrppyD) were formed in 39%, 49%, and 41% yield, respectively. These yields are over two steps and are based on the amount of iridium chloride trihydrate used in the first step. The final complexation step could lead to either facial or meridional isomers of the dendrimers. Under the conditions used in the final complexation step, from the iridium dimer to the tris complex, the *facial* isomer is normally formed. The *facial* nature of all three dendrimers was confirmed by ¹H NMR by comparison with the spectra reported for *fac*-Irppy₃ and *mer*-Irppy₃.^{21b,c}

Physical Properties. We first studied the physical properties of the dendrimers. All three dendrimers could

be spin-coated to form good-quality thin films. In addition, we found that the film-forming characteristics of the dendrimers could be extended to the formation of films containing blends of molecular materials such as 4,4'-bis(N-carbazolyl)biphenyl (CBP).9-11 Gel permeation chromatography (GPC) showed that 12, 13, and 14 were monodisperse. To estimate the hydrodynamic radii (R_h) of the dendritic ligands and dendrimers, we used the M_v determined by GPC and the Hester-Mitchell equation and Mark-Houwink relationship.²² The M_v 's of dendritic ligands **6**, **8**, and **11** and dendrimers 12, 13, and 14 were 743, 809 and 1481, and 2238, 3562 and 1681, respectively. These correspond to hydrodynamic radii of 5.4, 5.7, and 8.0 Å for 6, 8, and 11 and 10.2, 13.3, and 8.6 Å for 12, 13, and 14. For 3-G1-IrppyD (12), the increase in hydrodynamic volume was pprox 7 times that of the dendron. This is more than 2 times larger than might be expected for simply connecting three dendritic ligands to the iridium(III) cation. We believe that the larger than expected hydrodynamic volume is due to the more three-dimensional nature of the dendrimer imparted by the *facial* arrangement of the octahedral complex when compared with the dendron. For 3-G2-IrppyD (13), the increase in volume moving from dendron to dendrimer is \approx 4.5. This is closer to the expected increase in volume and is because the dendritic ligand is itself more three-dimensional in nature due to the larger number of nonplanar biphenyl units. However, for 4-G1-IrppyD (14), the increase in hydrodynamic volume in moving from the dendron to the dendrimer was only \approx 3.4. This value is close to the approximate 3-fold increase in volume that might be expected for connecting the dendritic ligands to the iridium cation and clearly demonstrates that the attachment point of the dendron has a significant effect on the three-dimensional shape of the dendrimers. The different three-dimensional shapes can clearly affect the morphology or packing of the dendrimers in a film.

Thermal gravimetric analysis was carried out at a heating rate of 10 °C/min under nitrogen. In each case no significant weight loss was seen below 300 °C, and even at 400 °C only a 5% weight loss was observed. This shows that the attachment of the dendrons to the 2-phenylpyridine iridium(III) core in either the 3- or 4-position of the phenyl group attached to the iridium does not have a detrimental effect on the thermal stability of the complex. The weight loss does not correspond to sublimation of the dendrimers. We also studied the thermal properties of the dendrimers by differential scanning calorimetry. We found that we needed fast scan rates of order 200-300 °C/min to observe the glass transition temperatures $(T_{g}s)$ of the dendrimers. The T_{gs} of 3-G1-IrppyD (12) and 3-G2-IrppyD (13) were found to be around 132 and 189 °C, respectively. The increase in T_g with generation is expected and follows the increase in dendrimer molecular weight. The first-generation dendrimer 4-G1-IrppyD (14) had a T_g at around 138 °C, and hence for the first-generation dendrimers the position to which the dendron is attached to the core complex has only a small effect on the thermal properties of the materials. Critically, the T_{g} s of all the dendrimers were sufficiently high to allow the formation of morphologically stable films suitable for device applications.

Photophysical Properties. The optoelectronic properties of the *fac*-(2-phenylpyridyl)iridium(III) complexes can be changed by the attachment of substituents to the



Figure 1. Solution UV-vis absorption spectra of Irppy₃, **12**, **13**, and **14** in toluene.

ligand.²³ We first compared the solution UV-vis absorption spectra of Irppy₃, 3-G1-IrppyD (12), and 3-G2-IrppyD (13) (Figure 1). The spectra of $Irppy_3$ can be divided into two regions. The first region at around 280 nm corresponds to absorption due to the π to π^* transitions of the ligands with the longer wavelength overlapping absorptions between 325 and 475 nm arising from the metal complex. The absorption at around 380 nm has been assigned to the metal to ligand singlet charge transfer state (MLCT¹).²⁴ On adding the biphenyl dendrons to the 3-position of the complex, there is little change in either the strength or position of the absorptions of the metal complex. However, there is a large change in the molar absorptivity in going from Irppy₃ to the first- and second-generation dendrimers 12 and 13 at around 280 nm. The increase in the molar extinction coefficient at this wavelength corresponds to the presence of the biphenyl units within the dendrons for 12 and 13 with the difference in absorptivity between 12 and 13 being due to the increased number of the biphenyl units in the second-generation dendrons. The fact that there is little change in the wavelength of the absorptions or molar absorptivities of the metal complex core for either generation illustrates that the meta arrangement around the branching phenyls to a first approximation breaks the conjugation both within the dendron and to the pyridine of the 2-phenylpyridyl ligand. In contrast for 4-G1-IrppyD (14) the first phenyl ring of the dendron is in conjugation with the pyridyl moiety in the ligand. The increased conjugation length gives rise to a small red shift, of order 18 nm, for the metal complex absorptions when compared to 12 and 13. The absorption spectra of the dendrimers were found to shift slightly in different solvents.

The solution photoluminescence (PL) spectra of Irppy₃, 3-G1-IrppyD (**12**), 3-G2-IrppyD (**13**), and 4-G1-IrppyD (**14**) are shown in Figure 2. For Irppy₃, **12**, and **13** the PL spectra all contain the same features, a peak at 514 nm and a shoulder at 545 nm. For **14** there was a small red shift of \approx 20 nm in the PL spectrum due to an increase in conjugation length caused by the first phenyl ring of the dendron being in conjugation with the pyridyl moiety via the phenyl ring of the ligand. The Commission Internationale de l'Eclairage (C.I.E.) coordinates for solution PL spectra for Irppy₃, **12**, and **13**



Figure 2. Solution photoluminescence spectra of Irppy₃, **12**, **13**, and **14** in toluene (excitation wavelength = 360 nm). The spectra have been normalized and offset vertically for clarity.



Figure 3. Film photoluminescence spectra of Irppy₃, **12**, **13**, and **14** (excitation wavelength = 325 nm).

are all (0.32, 0.62), and the red shift in the spectrum of 14 is reflected in coordinates of (0.38, 0.60). This again illustrates the importance of the connection point of the dendron to the ligand. The film PL spectra of Irppy₃ and the three dendrimers are shown in Figure 3. In going to the solid state, there is a significant difference in the emission spectra of the compounds. The PL spectrum of the neat film of Irppy₃ is featureless with the peak of the emission red-shifted by 30 nm. In addition, the spectrum contains a long red tail, which is at least in part due to aggregate emission.²⁵ The attachment of the first-generation dendron onto the Irppy₃ core in the 3-position causes the PL spectrum to look more like the emission spectrum in solution although the peak and shoulder are still red-shifted by around 15 nm with respect to the solution spectrum. The decrease in red shift of the spectrum relative to Irppy₃ is due to the dendrons on 12 decreasing the intermolecular interactions of the emissive cores within the film. Attachment of the second-generation dendron enhances the effect, and there is only a small difference between the solution and film PL spectra. For 14 which has the dendron in

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the 4-position rather than the 3-position, the change in the PL spectra is less in going from solution to the film than observed for **12**. The two peaks are still welldefined, and each is only shifted a small amount (4 nm) to the red. The C.I.E. coordinates further illustrate the movement of the color of the spectra with the coordinates of Irppy₃, **12**, and **13** being (0.41, 0.56), (0.36, 0.60), and (0.35, 0.61), respectively, and **14** having (0.42, 0.56). These results clearly show that the dendron generation and position of attachment assists in controlling the intermolecular interactions that can lead to changes in luminescence.

We probed these intermolecular interactions further by photoluminescence quantum yield (PLQY) measurements. For 3-G1-IrppyD (12) and 3-G2-IrppyD (13) it was found that the PLQY of the second-generation dendrimer at 31% was approximately 1.5 times higher than the first generation.^{9,10} This is consistent with reduced intermolecular core-core interactions for the second-generation dendrimer. However, we have measured the PLQY of both **12** and **13** in degassed toluene and found them to be 70% and 69%, respectively, which indicates that even with the second-generation dendrimer there are still significant intermolecular interactions in the film that cause PL quenching. For 4-G1-IrppyD (14) the solution PLQY was 74% and the film PLQY was 24%.¹¹ The decrease in PLQY is similar to that seen for 3-G1-IrppyD (12). By using the dendrimer in a host matrix, the detrimental intermolecular interactions can be controlled. For example, when 20 wt % of 3-G1-IrppyD (**12**) was incorporated into a CBP host, the PLQY was found at 78% to be similar to the solution PLQY.¹⁰ When 3-G2-IrppyD (13) and 4-G1-IrppyD (14)¹¹ were blended with CBP at the same weight percent, the measured PLQYs were 80% and 68%. For the PLQY measurement of the blends the excitation wavelength of 325 nm excited both the CBP host and the dendrimer guests. However, PL emission was only observed from the dendrimers, indicating efficient energy transfer from the CBP host to the dendrimer guests. Therefore, the fact that the PLQY of the films is at least as high as the solution measurements indicates that in the solid solution of the film the dendrimers are not aggregating. The remarkable aspect of these blend films is that it is the dendrimers that provide the good film-forming properties even though they are the minority component in the blend. A final aspect of the PL study was to determine whether energy could be transferred efficiently from the dendrons to the core. For all three dendrimers the film UV-vis absorption and photoluminescence excitation (PLE) spectra were collected with that of 4-G1-IrppyD (14) shown in Figure 4 by way of example. For 14 the emission was observed at 540 nm, and the excitation wavelength was scanned from 700 to 260 nm. As expected, the direct excitation of the core metal complex (325–425 nm) gives rise to efficient core luminescence. In addition, the PLE spectrum matches the absorption spectrum at short wavelengths where the dendrons and the ligands absorb. This shows that energy absorbed by the biphenyl units in the dendrons is transferred to the core. If energy was not transferred efficiently from the dendrons to the core, then the PLE spectrum would mirror the absorption spectrum of the core complex and hence look similar to the absorption spectrum of Irppy₃ in Figure 1. For **12** and **13** the PLE spectra also followed their respective UV-vis absorption spectra closely over both wavelength ranges. This



Figure 4. Film UV–vis absorption and photoluminescence excitation spectra (PLE) (observed at 540 nm) of **14**.

indicates that energy transfer from the dendrons to the core was independent of the point of attachment of the dendrons to the core and, at these low generations, the generation.

Electrochemical Properties. The final part of the study on the materials was electrochemical analysis of their electronic properties. Although the PLE spectra indicated that energy transfer from the dendrons to the core was efficient, their wide band gap suggests that charge should be injected directly in the organometallic core. The cyclic voltammagrams of the three dendrimers are shown in Figure 5. 3-G1-IrppyD (12) had one chemically reversible oxidation at 0.24 V and three chemically reversible reductions at -2.91, -3.10, and -3.28 V. Each of the redox processes corresponded to one electron, and the potentials at which the oxidation and reductions of **12** occurred were essentially the same as those reported for Irppy₃.²³ The electrochemical results in conjunction with the optical studies show that the attachment of the dendrons in the 3-position or para to the metal carbon bond does not change the absolute energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) or the HOMO-LUMO energy gap appreciably. During this study we were surprised to find that the singly oxidized 12 was remarkably stable to oxygen and moisture during the electrochemical experiment. The electrochemical experiments were normally carried out under anhydrous conditions and an inert atmosphere, but we found that even after the addition of water and allowing air into the cell the oxidation of 12 was still chemically reversible. In contrast, the reduction processes of **12** were very sensitive to moisture and oxygen. For 3-G2-IrppyD (13) and 4-G1-IrppyD (14) the chemically reversible oxidations were easily seen at 0.26 and 0.27 V. The oxidation potentials of 12, 13, and 14 are similar despite the slight red shift (0.1 eV in the PL spectra). This can be understood by the fact that the HOMO of iridium(III) complexes contains substantial iridium character^{21c} which does not change significantly between the three dendrimers. In contrast, the LUMO for this type of iridium(III) complex is comprised of the π^* orbitals^{21c} of the ligand, and therefore the red shift in the PL emission for 14 must be due to a decreased LUMO energy leading to a more positive reduction potential. However, under identical conditions used for



Figure 5. (a) Oxidation cyclic voltammograms of **12**, **13**, and **14**. Scan rate = 40 mV/s, solvent = dichloromethane, concentration = 1 mM, platinum working electrode. (b) Reduction cyclic voltammogram of **12**. Scan rate = 120 mV/s, solvent = tetrahydrofuran, concentration = 1 mM, glassy carbon working electrode.

12 we were unable to observe clear chemically reversible reductions for **13** and **14**. Indeed for **14** on applying a negative switching potential (\approx -3.6 V) a dark green compound was observed to form near the working electrode, suggesting that a chemically irreversible process was occurring. A final interesting observation from the electrochemical study was that the difference between the $E_{1/2}$ of the first oxidation and reduction for **12** was 3.15 V, and this corresponds to the absorption wavelength (394 nm) of the MLCT¹ in the absorption spectrum. This indicates that charge can be injected directly into the orbitals associated with the MLCT singlet state.

Conclusion

We have developed a simple synthetic route to solution processable iridium complex cored dendrimers that have been demonstrated to give highly efficient OLEDs. We have demonstrated that the dendrons can be used to give processability to molecular materials and can control the important intermolecular interactions for phosphorescent dendrimers in a manner similar to fluorescent dendrimers. The dendrimers are thermally stable, and photoluminescence excitation experiments show that energy can be transferred efficiently from the dendrons to the emissive core whereas cyclic voltammetry reveals that charge is injected directly into the core.

Experimental Section

Measurements. NMR spectra were recorded on Bruker DPX 400 MHz, AMX 500 MHz, or Varian Gemini 200 MHz spectrometers: sp = surface phenyl; bp = branch phenyl; L = ligand. All J values are in hertz. UV-vis spectra were recorded on a Perkin-Elmer UV-vis Lambda 14P spectrometer and were recorded as solutions in toluene or spectroscopic grade dichloromethane. Mass spectra were recorded on a VG Autospec for EI or a Micromass TofSpec 2E for matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) from dithranol (DITH) or 2,5-dihydroxybenzoic acid (DHB) in reflectron mode or a VG Platform for APCI. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were carried out in the Inorganic Chemistry Laboratory, Oxford, UK. Gel permeation chromatography was carried out using PLgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards (M_p = 580 to 3.2×10^6) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed with helium and pumped at a rate of 1 mL/min at 30.0 °C. Thermal gravimetric analysis was performed on a Perkin-Elmer thermogravimetric analyzer TGA 7. Glass transition temperatures were measured on a Perkin-Elmer differential scanning calorimeter Pyris 1. Light petroleum refers to the fraction of boiling point 40-60 °C, unless otherwise stated. When solvent mixtures are used for chromatography over silica, the proportions are given by volume.

Electrochemistry was performed using an EG&G Princeton Applied Research potentiostat/galvanostat model 263A. All measurements were made at room temperature on samples dissolved in dichloromethane or tetrahydrofuran, with 0.1 M tetra-n-butylammonium tetrafluoroborate as the electrolyte. The tetrahydrofuran was distilled from sodium wire and benzophenone under argon and then distilled from lithium aluminum hydride under argon. HPLC grade dichloromethane was used for the oxidation studies. The electrolyte was purified by recrystallization from ethyl acetate. The solutions were deoxygenated with argon. A glassy carbon or platinum working electrode, platinum wire counter electrode, and Ag/3 M NaCl/ AgCl(sat) reference electrode was used. The ferricenium/ ferrocene couple was used as standard,²⁶ and the ferrocene was purified by sublimation or recrystallization from ethanol. All potentials are quoted relative to the ferricenium/ferrocene couple. In all cases several scans were carried out to confirm the chemical reversibility of the redox processes.

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 0.51, as the standard.²⁷ The dendrimers were dissolved in toluene and freeze—thaw degassed. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the dendrimer 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 $\pm 10\%$.

Films were spin-coated from chloroform solutions with a dendrimer concentration of 10 mg/mL at 900 rpm for 1 min to give a thickness of about 150 nm. Their PLQY was measured using an integrating sphere in accordance with Greenham *et al.*²⁸ using a Helium Cadmium laser (Kimmon) as the excitation source. The excitation power was 0.05 mW at 325 nm and the sphere was purged with nitrogen.

G0-B(OCMe₂)₂ (2). *tert*-Butyllithium (1.5 M, 3.8 mL, 5.66 mmol) was added to a solution of 1-bromo-4-(2'-ethylhexyloxy)-

benzene¹⁸ (1) (1.01 g, 3.54 mmol) in anhydrous tetrahydrofuran (7 mL) that had been cooled in an dry ice/acetone bath under argon. The mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.87 mL, 4.26 mmol) was added rapidly to the cold mixture, and the mixture was stirred at -78 °C for 2 h. The mixture was allowed to warm room temperature and then stirred at room temperature for 65 h. The reaction was quenched with water (3 mL), and the two layers were separated. The aqueous layer was extracted with ether (3 \times 7 mL), and then the organic layer and the ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The solvent was completely removed and the residue purified by column chromatography over silica gel using ethyl acetate-light petroleum (0:1 to 1:10) as eluent to give 2 (806 mg, 69%). Anal. Calcd for C20H33BO3: C, 72.3; H, 10.0. Found: C, 72.15; H, 10.05. λ_{max} (CH₂Cl₂)/nm: 244 (log $\epsilon/dm^3~mol^{-1}~cm^{-1}$ 4.33), 271 (3.15), and 282 (2.98). $\delta_{\rm H}$ (400.1 MHz; CDCl₃): 0.87-0.97 (6 H, m, Me), 1.30-1.58 (20 H, m, CH₂ and Me), 1.70–1.78 (1 H, m, CH), 3.88 (2 H, m, ArOCH₂), 6.91 and 7.76 (4 H, AA'BB', ArH). δ_C (100.6 MHz; CDCl₃): 11.1, 14.1, 23.0, 23.8, 24.8, 29.0, 30.5, 39.3, 70.2, 83.5, 113.9, 136.4, and 162.0. m/z [EI] 332.3 (M⁺).

G1-Br (3). A mixture of 2 (380 mg, 1.14 mmol), 1,3,5tribromobenzene (163 mg, 0.520 mmol), tetrakis(triphenylphosphine)palladium(0) (33 mg, 0.029 mmol), aqueous sodium carbonate (2 M, 0.5 mL), ethanol (0.5 mL), and toluene (1.5 mL) was deoxygenated and then heated at reflux under argon for 24 h. The mixture was allowed to cool, and water (3 mL) and ether (4 mL) were added. The organic layer was removed, and the aqueous layer was extracted with ether (3 \times 5 mL). The organic layer and the ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by column chromatography over silica gel using dichloromethanelight petroleum (0:1 to 1:10) as eluent to give 3 (202 mg, 60%). Anal. Calcd for C₃₄H₄₅BrO₂: C, 72.2; H, 8.0. Found: C, 71.85; H, 7.9. λ_{max} (CH₂Cl₂)/nm: 274 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.70). δ_{H} (400.1 MHz; CDCl₃): 0.87-1.03 (12 H, m, Me), 1.32-1.63 (16 H, m, CH₂), 1.76-1.86 (2 H, m, CH), 3.93 (4 H, m, ArOCH₂), 7.03 and 7.56 (8 H, AA'BB', sp H), and 7.66 (3 H, m, G1-bp H). δ_C (100.6 MHz; CDCl₃): 11.2, 14.2, 23.1, 23.9, 29.1, 30.5, 39.4, 70.5, 114.9, 123.2, 123.9, 127.8, 128.2, 132.0, 143.3, and 159.5. m/z [MALDI: DHB] 564.4 and 566.3 (M⁺). 1,3,5-Tri[4'-(2"-ethylhexyloxy)phenyl]benzene (96 mg, 27%) was also isolated. $\delta_{\rm H}$ (200 MHz; CDCl₃): 0.82–1.02 (18 H, m, Me), 1.25– 1.63 (24 H, m, CH₂₎, 1.70–1.83 (3 H, m, CH), 3.90 (6 H, d. J= 5.5, ArOCH₂), 7.01 and 7.62 (12 H, AA'BB', sp H), and 7.65 (3 H, s, cp H). *m*/*z* [APCI⁺] 691.5 (MH⁺).

G1-B(OCMe₂)₂ (4). tert-Butyllithium (1.5 M, 4.8 mL, 7.2 mmol) was added to a solution of 3 (2.02 g, 3.57 mmol) in anhydrous ether (12 mL) that had been cooled in a dry ice/ acetone bath under argon. The mixture was stirred at -78 °C for 1.5 h, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2dioxaborolane (0.9 mL, 4.4 mmol) was added rapidly to the mixture. The mixture was allowed to warm to room temperature over 3 h and then stirred at room temperature for further 62 h before being quenched with water (5 mL). The organic layer was removed, and the aqueous layer was extracted with ether $(3 \times 5 \text{ mL})$. The organic layer and the ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by column chromatography over silica gel using ethyl acetate-light petroleum (1:10) and then ethyl acetate-light petroleum (0:1 to 1:30) as eluent to give 4 (1.63 g, 75%). Anal. Calcd for C40H57BO4: C, 78.4; H, 9.4. Found: C, 78.4; H, 9.4. λ_{max} (CH₂Cl₂)/nm: 269 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.61). δ_H (500.0 MHz; CDCl₃): 0.91-1.00 (12 H, m, Me), 1.31-1.64 (28 H, m, CH₂ and Me), 1.73-1.82 (2 H, m, CH), 3.91 (4 H, m, ArOCH₂), 7.00 and 7.63 (8 H, AA'BB', sp H), 7.85 (1 H, m, G1-bp H), and 7.97 (2 H, m, G1-bp H). $\hat{\delta}_{C}$ (125.7 MHz; CDCl₃): 11.0, 14.0, 23.0, 23.8, 24.8, 29.0, 30.4, 39.3, 70.5, 83.8, 114.6, 128.0, 128.2, 131.3, 133.3, 140.7, and 158.9. m/z [EI] 612.3 (M⁺).

3-G1-Lig (6). A mixture of **4** (100 mg, 0.163 mmol), 2-(3'bromophenyl)pyridine (**5**)¹⁹ (32 mg, 0.137 mmol), tetrakis-

(triphenylphosphine)palladium(0) (11 mg, 0.010 mmol), aqueous sodium carbonate (2 M, 0.1 mL), ethanol (0.1 mL), and toluene (0.3 mL) was deoxygenated and then heated at reflux under argon for 20 h. The mixture was allowed to cool to room temperature, and water (4 mL) and ether (4 mL) were added. The organic layer was removed, and the aqueous layer was extracted with ether (3 \times 5 mL). The organic layer and the ether extracts were combined, washed with brine (8 mL), dried over anhydrous sodium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by chromatotron over silica gel using dichloromethane-light petroleum (1:50 to 1:10) as eluent to give 6 (87 mg, 99%). Anal. Calcd for C45H53NO2: C, 84.5; H, 8.4; N, 2.2. Found: C, 84.2; H, 8.5; N, 2.2. λ_{max} (CH₂Cl₂)/nm: 270 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.84). $\delta_{\rm H}$ (400.1 MHz; CDCl₃): 0.92–1.03 (12 H, m, Me), 1.32– 1.67 (16 H, m, CH₂), 1.76-1.86 (2 H, m, CH), 3.95 (4 H, m, ArOCH2), 7.06 and 7.68 (8 H, AA'BB', sp H), 7.28 (1 H, m, L H), 7.62 (1 H, t, J = 7.5, L H), 7.75–7.88 (6 H, m, L H and G1-bp H), 8.05 (1 H, d, J = 7.8, L H), 8.37 (1 H, d, J = 1.6, L H), and 8.77 (1 H, m, L H). δ_C (100.6 MHz; CDCl₃): 11.2, 14.1, 23.1, 23.9, 29.1, 30.6, 39.4, 70.6, 114.9, 120.7, 122.2, 124.3, 124.5, 126.0, 128.0, 128.3, 129.2, 133.4, 136.8, 140.0, 141.97, 141.99, 142.1, 149.7, 157.4, and 159.2. m/z [APCI+] 640.5 (MH^+)

4-G1-Lig (8). A mixture of 4 (100 mg, 0.163 mmol), 2-(4'bromophenyl)pyridine (7)¹⁸ (32 mg, 0.137 mmol), tetrakis-(triphenylphosphine)palladium(0) (11 mg, 0.010 mmol), aqueous sodium carbonate (2 M, 0.1 mL), ethanol (0.1 mL), and toluene (0.3 mL) was deoxygenated and then heated at reflux under argon for 21.5 h. The mixture was allowed to cool to room temperature, and water (4 mL) and ether (5 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ether $(3 \times 5 \text{ mL})$. The organic layer and the ether extracts were combined, washed with brine (10 mL), dried over anhydrous sodium sulfate, and filtered, and then the solvents were completely removed. The residue was purified by chromatotron over silica gel using dichloromethanelight petroleum (0:1 to 1:20) as eluent to give **8** (87 mg, 100%) as a colorless oil, which crystallized on standing; mp 97-98 °C. Anal. Calcd for C45H53NO3: C, 84.5; H, 8.4; N, 2.2. Found: C, 84.1; H, 8.3; N, 2.3. λ_{max} (CH₂Cl₂)/nm 283 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.81). $\delta_{\rm H}$ (400.1 MHz; CDCl₃): 0.94–1.03 (12 H, m, Me), 1.32-1.64 (16 H, m, CH₂), 1.77-1.88 (2 H, m, CH), 3.90-3.97 (4 H, m, ArOCH₂), 7.05 and 7.66 (8 H, AA'BB', sp H), 7.27 (1 H, m, L H), 7.75-7.85 (7 H, m, G1-bp H and L H), 8.15 (2 H, 1/2AA'BB', L H), and 8.76 (1 H, m, L H). δ_{C} (100.6 MHz; CDCl₃): 11.1, 14.1, 23.1, 23.9, 29.1, 30.5, 39.4, 70.5, 114.8, 120.5, 122.2, 124.0, 127.3, 127.7, 128.3, 133.4, 136.8, 138.4, 141.6, 141.8, 142.1, 149.7, 157.0, and 159.2. m/z [APCI+] 640.4 (MH⁺).

Lig-B(OCMe₂)₂ (9). tert-Butyllithium (1.7 M, 36.6 mL, 62 mmol) was added to a solution of 2-(3'-bromophenyl)pyridine (5)¹⁹ (8.10 g, 34.6 mmol) in anhydrous tetrahydrofuran (130 mL) that had been cooled in a dry ice/acetone bath under argon. The mixture was stirred at -78 °C for 2 h, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9 mL) was added rapidly to the cold mixture. The reaction was stirred at -78 °C for 2 h, allowed to warm to room temperature, and then stirred at room temperature for further 20 h. The reaction was quenched with water (30 mL), and the organic layer was removed. The aqueous layer was extracted with ether (3×40) mL). Saturated sodium bicarbonate solution (40 mL) was then added to the aqueous layer, and then the aqueous layer was extracted with ether (2 \times 40 mL). The organic layer and the ether extracts were combined, dried over anhydrous sodium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by column chromatography over silica gel using dichloromethane-light petroleum (0:1 to 1:30) as eluent to give 9 (4.92 g, 50%). Anal. Calcd for $C_{17}H_{20}$ -BNO₂: C, 72.6; H, 7.2; N, 5.0. Found: C, 72.6; H, 7.2; N, 5.0. λ_{max} (CH₂Cl₂)/nm 250 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.08) and 279 (4.04). $\delta_{\rm H}$ (400.1 MHz; CDCl₃): 1.37 (12 H, s, Me), 7.23 (1 H, m, PyH), 7.51 (1 H, m, PhH), 7.76 (1 H, m, PyH), 7.80 (1 H, m, PyH), 7.87 (1 H, m, PhH), 8.14 (1 H, m, PyH), 8.40 (1 H, m, PhH), and 8.71 (1 H, m, PyH). δ_C (100.6 MHz; CDCl₃): 24.9,

83.9, 120.7, 122.0, 128.2, 129.9, 133.2, 135.3, 136.6, 138.7, 149.6, 154.6, and 157.5. *m*/*z* [APCI⁺] 282.2 (MH⁺).

Lig-DiBrPh (10). A mixture of the 9 (5.15 g, 18.3 mmol), 1,3,5-tribromobenzene (6.92 g, 22.0 mmol), tetrakis(triphenylphosphine)palladium(0) (846 mg, 0.732 mmol), aqueous sodium carbonate (2 M, 12 mL), ethanol (12 mL), and toluene (48 mL) was deoxygenated and then heated at reflux under argon for 19.5 h. The mixture was allowed to cool, and water (10 mL) and ether (20 mL) were added. The organic layer was removed, and the aqueous layer was extracted with ether (3 \times 20 mL). The organic layer and the ether extracts were combined, dried over anhydrous sodium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by column chromatography over silica gel using ethyl acetate-light petroleum (0:1 to 1:20) as eluent to give 8 (4.70 g, 66%). Anal. Calcd for C17H11Br2N: C, 52.5; H, 2.9; N, 3.6. Found: C, 52.6; H, 2.5; N, 3.6. λ_{max} (CH₂Cl₂)/nm 249 (log ϵ /dm³ mol $^{-1}$ cm $^{-1}$ 4.50) and 274 sh (4.32). $\delta_{\rm H}$ (400.1 MHz; CDCl_3): 7.29 (1 H, m, L H), 7.57 (2 H, m, L H), 7.67 (1 H, t, J = 1.7, G1-bp H), 7.75 (2 H, d, J = 1.7, G1-bp H), 7.79 (2 H, m, L H), 7.99 (1 H, m, L H), 8.19 (1 H, m, L H), and 8.74 (1 H, m, L H). δ_C (100.6 MHz; CDCl₃): 120.7, 122.5, 123.2, 125.7, 126.9, 127.6, 129.1, 129.4, 132.7, 136.9, 138.9, 140.2, 144.6, 149.8, and 156.8. m/z [APCI] 388.0 (MH+).

3-G2-Lig (11). A mixture of 4 (132 mg, 0.215 mmol), 10 (30 mg, 0.077 mmol), tetrakis(triphenylphosphine)palladium(0) (7 mg, 6 µmol), aqueous sodium carbonate (2 M, 0.1 mL), ethanol (0.1 mL), and toluene (0.3 mL) was deoxygenated and then heated at reflux under argon for 18 h. The mixture was allowed to cool to room temperature, and water (4 mL) and ether (5 mL) were added. The organic layer was removed, and the aqueous layer was extracted with ether (3 \times 5 mL). The organic layer and the ether extracts were combined, washed with brine (8 mL), dried over anhydrous sodium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by chromatotron over silica gel using dichloromethane-light petroleum (0:1 to 1:4) as eluent to give 11 (91 mg, 98%). Anal. Calcd for C₈₅H₁₀₁NO₄: C, 85.0; H, 8.5; N, 1.2. Found: C, 84.8; H, 8.7; N, 1.1. λ_{max} (CH₂Cl₂)/nm 270 (log ϵ /dm³ mol⁻¹ cm⁻¹ 5.27). $\delta_{\rm H}$ (400.1 MHz; CDCl₃): 0.92– 1.02 (24 H, m, Me), 1.33-1.60 (32 H, m, CH₂), 1.74-1.84 (4 H, m, CH), 3.94 (8 H, m, ArOCH2), 7.05 (8 H, 1/2AA'BB', sp H), 7.28 (1 H, m, L H), 7.62-7.73 (9 H, m, sp H and L H), 7.77-7.89 (9 H, m, G2-bp H and L H), 8.02 (3 H, m, G1-bp H), 8.07 (1 H, d, J = 7.9, ArĤ), 8.38 (1 H, m, L H), and 8.76 (1 H, s, L H). δ_C (101.6 MHz; CDCl₃): 11.1, 14.1, 23.1, 23.9, 29.1, 30.5, 39.4, 70.5, 114.9, 120.8, 122.3, 124.4, 124.7, 125.7, 126.1, $126.2,\ 128.0,\ 128.4,\ 129.4,\ 133.3,\ 136.8,\ 140.1,\ 141.6,\ 142.1,$ 142.2, 142.4, 142.7, 149.7, 157.3, and 159.2. m/z [MALDI: DITH] 1200.6 (MH⁺).

3-G1-IrppyD (12). A mixture of 6 (294 mg, 0.459 mmol), iridium chloride trihydrate (41 mg, 0.12 mmol), water (1.0 mL), and 2-ethoxyethanol (3.0 mL) was heated (bath temperature: 125-135 °C) under argon for 39 h. After cooling, the resultant mixture was passed through a column of silica gel using ethyl acetate-light petroleum (0:1 to 1:10), dichloromethane, and then methanol as eluents. The filtrate was collected (≈600 mL) and concentrated to about 50 mL. An orange-yellow solid precipitated and was collected by filtration. The residue was washed with methanol (\approx 10 mL). The bright yellow solid was dried (177 mg) and then reprecipitated from a dichloromethane-methanol mixture to give impure iridium dimer (125 mg). Excess 5 was collected from the filtrate, and the two products were used without further purification for the next step. A mixture of the above-obtained iridium complex, recycled 5, and silver trifluoromethanesulfonate (34 mg, 0.133 mmol) was heated (bath temperature: 130 °C) for 3.5 days under argon. The reaction was then allowed to cool to room temperature, and the mixture was purified by column chromatography over silica gel using dichloromethane-ethyl acetate-light petroleum (0:1:10 to 1:1:10) as eluent to give 12 (95 mg, 39%), TGA_(5%) 400 °C. T_g 132 °C (scan rate = 200 °C/ min). Anal. Calcd for $C_{135}H_{156}Ir\breve{N}_{3}O_{6}\!\!:$ C, 76.9; H, 7.5; N, 2.0. Found: C, 76.7; H, 7.2; N, 2.1. λ_{max} (CH₂Cl₂)/nm 279 (log ϵ /dm³ mol⁻¹ cm⁻¹ 5.26), 325 sh (4.69), 389 sh (4.17), 414 sh (4.01), 458 sh (3.55), and 488 sh (3.16). $\delta_{\rm H}$ (400.1 MHz; CD₂Cl₂): 0.92– 1.03 (36 H, m, Me), 1.31–1.66 (48 H, m, CH₂), 1.73–1.86 (6 H, m, CH), 3.95 (12 H, m, ArOCH₂), 7.00–7.13 (18 H, m, sp H and L H), 7.30 (3 H, m, L H) 7.67–7.83 (27 H, m, sp H, G1-bp H, and L H), 8.10 (3 H, d, J = 1.7, L H), and 8.15 (3 H, d, J =8.4, L H). $\delta_{\rm C}$ (100.6 MHz; CDCl₃): 11.7, 14.7, 23.9, 24.6, 29.9, 31.3, 40.2, 71.35, 115.5, 120.0, 123.4, 123.6, 123.8, 124.2, 129.0, 129.7, 134.0, 134.3, 137.4, 138.1, 142.5, 144.1, 145.4, 148.2, 160.0, 161.5, and 167.0; m/z [MALDI: DITH] Anal. Calcd for C₁₃₅H₁₅₆IrN₃O₆: 2106.2 (30%), 2107.2 (48%), 2108.2 (89%), 2109.2 (100%), 2110.2 (70%), 2111.2 (34%), 2112.2 (15%), 2108.3 (100%), 2109.3 (100%), 2110.3 (77%), 2111.4 (38%), 2112.4 (18%), 2113.4 (7%) (M⁺). In addition excess **6** (121 mg) was recovered.

3-G2-IrppyD (13). A mixture of 11 (2.97 g, 2.47 mmol), iridium chloride trihydrate (174 mg, 0.50 mmol), water (4 mL), and 2-ethoxyethanol (13 mL) was heated (bath temperature: 107 °C) under argon for 60 h before being allowed to cool. The resultant precipitate was collected by filtration and purified by column chromatography over a silica gel using dichloromethane-light petroleum (1:30 to 1:10) as eluent to give the chloro-bridged iridium dimer (900 mg). 11 (1.96 g) was recovered from the filtrate after purification by column chromatography over silica gel using ethyl acetate-light petroleum (1:30 to 1:10) as eluent. A mixture of the chloro-bridged iridium dimer (900 mg), 11 (1.96 g), and silver trifluoromethanesulfonate (300 mg, 1.17 mmol) was heated (bath temperature: 145 °C) under argon for 7 days. The reaction was allowed to cool to room temperature, and the mixture was purified by column chromatography over silica gel using dichloromethanelight petroleum (1:20) as eluent to give 13 (774 mg, 41%), $TGA_{(5\%)}$ 400 °C. T_g 189 °C (scan rate = 300 °C/min). Anal. Calcd for C₂₅₅H₃₀₀IrN₃O₁₂: C, 80.8; H, 8.0; N, 1.1. Found: C, 80.7; H, 8.0; N, 1.1. λ_{max} (CH₂Cl₂)/nm 272 (log ϵ /dm³ mol⁻¹ cm⁻¹ 5.64), 336 sh (4.76), 388 sh (4.22), 413 sh (4.06), 458 sh (3.57), and 488 sh (3.18). $\delta_{\rm H}$ (400.1 MHz; CD₂Cl₂): 0.90–1.00 (72 H, m, Me), 1.30-1.61 (96 H, m, CH₂), 1.70-1.83 (12 H, m, CH), 3.91 (24 H, m, ArOCH₂), 7.00-7.12 (30 H, sp H and L H), 7.22 (3 H, d, J = 7.9, L H), 7.43 (3 H, m, L H), 7.70-7.77 (27 H, m, sp H and L H), 7.77 (3 H, m, L H), 7.82 (6 H, s, G2-bp H), 7.93 (12 H, s, G2-bp H), 8.02 (3 H, s, G1-bp H), 8.09 (6 H, s, G1-bp H), and 8.18 (6 H, m, L H). m/z [MALDI: DITH] 3791 (broad) (M⁺). In addition excess **11** (676 mg) was recovered.

4-G1-IrppyD (14). A mixture of 8 (490 mg, 0.766 mmol), iridium chloride trihydrate (68 mg, 0.19 mmol), water (1.6 mL), and 2-ethoxyethanol (4.9 mL) was heated (bath temperature: 130 °C) under argon for 28 h before being allowed to cool. The mixture was purified by column chromatography over silica using ethyl acetate-light petroleum (0:1 to 1:10) and then dichloromethane as eluent. The fractions containing the chlorobridged iridium dimer and excess ligand were combined, and the solvent was completely removed. The residue was dissolved in dichloromethane (2 mL), and methanol (2 mL) was added. The chloro-bridged dimer that precipitated was collected (\approx 238 mg) and used without further purification for the next step. The solvent was removed from the filtrate to give crude unreacted ligand (≈244 mg). A mixture of the chloro-bridged dimer, recycled crude ligand 8 (~244 mg), fresh 8 (200 mg, 0.313 mmol), and silver trifluoromethanesulfonate (70 mg, 0.27 mmol) was heated (bath temperature: 130-140 °C) for 88 h under argon. The reaction was allowed to cool to room temperature, and the mixture was purified by column chromatography over silica gel using dichloromethane-ethyl acetate-light petroleum mixture (0:1:10 to 1:1:10) as eluent to give 14 (200 mg, 49%) as an orange-yellow solid; TGA_(5%) 410 °C; T_g 138 °C (scan rate = 250 °C/min). Anal. Calcd for $C_{135}H_{156}$ -IrN3O6: C, 76.9; H, 7.5; N, 2.0. Found: C, 76.8; H, 7.5; N, 2.0.; $\lambda_{\rm max}$ (CH₂Cl₂)/nm 265 sh (log ϵ /dm³ mol⁻¹ cm⁻¹ 5.26), 282 (5.29), 391 (4.24), 436 sh (3.83), 472 sh (3.54), and 510 sh (2.86). $\delta_{\rm H}$ (400.2 MHz; CDCl₃): 0.90-0.97 (36 H, m, Me), 1.29-1.55 (48 H, m, CH₂), 1.61-1.70 (6 H, m, CH), 3.66-3.72 (12 H, m, ArOCH₂), 6.62 and 7.37 (24 H, AA'BB', sp H), 6.87 (3 H, m, L H), 7.41 (3H, m, L H), 7.50-7.60 (9 H, m, G1-bp H and L H), 7.68 (6 H, s, G1-bp H), 7.75-7.80 (6 H, m, L H), and 7.87 (1

H, d, J = 8.3, L H). $\delta_{\rm C}$ (100.6 MHz; CDCl₃): 11.2, 14.2, 23.1, 23.8, 29.1, 30.5, 39.4, 70.2, 114.4, 118.7, 119.0, 122.0, 123.4, 123.7, 124.7, 127.8, 133.3, 135.7, 135.9, 141.37, 141.43, 142.6, 143.5, 147.3, 158.8, 162.0, and 166.4; m/z [MALDI: DITH]. Anal. Calcd for C₁₃₅H₁₅₆IrN₃O₆: 2106.2 (37%), 2107.2 (57%), 2108.2 (95%), 2109.2 (100%), 2110.2 (81%), 2111.3 (40%), 2112.3 (17%), 2113.5 (5%). Found: 2106.2 (35%), 2107.1 (55%), 2108.3 (93%), 2109.2 (100%), 2110.2 (78%), 2111.3 (41%), 2112.3 (18%), 2113.4 (5%) (M⁺).

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