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Investigating the Effect of Steric Crowding in Phosphorescent Dendrimers

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ABSTRACT: A simple convergent procedure has been developed for the formation of sterically encumbered phosphorescent dendrimers. The procedure is demonstrated with the preparation of a first-generation dendrimer composed of a *fac*-tris(2-phenylpyridyl)iridium(III) core and three dendrons. Each dendron is comprised of a branching phenyl unit with a further four phenyl groups attached. The lack of surface groups on the dendrons was found to reduce solubility and also reduced the level of control over the intermolecular interactions of the emissive and electroactive core in films. The 6-fold decrease in photoluminescence quantum yield in going from solution (69%) to the solid state (11%) showed that there were strong intermolecular interactions of the emissive cores in the solid state. Single-layer devices with the dendrimer blended with 4,4′-bis(*N*-carbazolyl)biphenyl showed an external quantum efficiency of 1.7% (5.4 cd/A) at 100 cd/m^2 and 11.4 V, giving a power efficiency of 1.5 lm/W.

Introduction

Intermolecular interactions play a key role in organic light-emitting diodes (OLEDs). While strong intermolecular interactions between the electroactive chromophores are good for charge transport, they can be detrimental to light emission. Close interactions of emissive chromophores can lead to emission from excimers or aggregates leading to a change in emission color and generally lower photoluminescence quantum yields (PLQYs). The tradeoff between these two properties is clearly seen with small phosphorescent molecules when used in OLEDs. Reports on OLEDs based on phosphorescent small molecules have generally shown that devices are more efficient when the phosphorescent molecule is a guest in a host matrix.[1,2] At low concentration of phosphorescent molecules, there are few intermolecular interactions of the emissive species and the device efficiency is high. However, in blended systems, whether evaporated or solution processed, there is always the issue of how evenly distributed the guest is in the host as localized high concentrations can lead to poor device performance. The most efficient method of controlling molecular interactions is by building in the control at the molecular level. This is difficult to do with small molecules, and with polymeric materials understanding the intermolecular interactions is complicated by the often complex polymer morphology.[3,4] Dendrimer light-emitting diodes (DLEDs) are developing into an exciting class of OLEDs.[5−10] Light-emitting dendrimers have mainly been designed with a light-emitting chromophore at the core to which one or more dendrons are attached. Surface groups are generally placed at the distal ends of the dendrons to provide the required processing properties. One of the key features of light-emitting dendrimers is that by having the emissive and electroactive chromophore at the core the intermolecular interactions can be controlled at the molecular level by either the number of dendrons attached to the core or the dendrimer generation. By judicious positioning of the dendrons this can be done without changing the emissive properties of the core chromophore.[9,10] Recent reports have shown that the dendritic approach can be used to develop solution processable phosphorescent materials that give rise to highly efficient green and red DLEDs.[10,11] The green emissive dendrimers developed had 2-ethylhexyl surface groups, phenyl-based dendrons, and *fac*-tris(2-phenylpyridyl)iridium(III) cores.[10,12] It was found that with these dendrimers increasing the dendrimer generation decreased the charge mobility[13] through the film but improved the solid-state photoluminescence quantum yield with a net improvement in DLED performance.[14] However, the degree of branching in these dendrimers close to the emissive chromophore is relatively low, and it was therefore of interest to see whether the same level of control over intermolecular interactions can be gained by increasing the degree of branching but at lower generation. In our work we have found that the rigidity imparted by conjugated dendrons gives better control over the intermolecular interactions and makes identifying the structure−property relationships more straightforward. The most highly branched conjugated dendrons that are easily accessed are those based on biphenyl units, which have been developed by Müllen and co-workers.[15] Given that the first branching point in a “Müllen” dendron is a phenyl unit as in the earlier phosphorescent dendrimers,[10,11] they are the natural choice of dendron for comparing the effect of the level of branching on controlling the intermolecular interactions of *fac*-tris(2-phenylpyridyl)iridum(III) cored dendrimers.

In this paper we describe the synthesis of a first-generation dendrimer containing a Müllen dendron attached to each ligand of the *fac*-tris(2-phenylpyridyl)-iridium(III) core (**6**, Scheme 1). In **6** the branching phenyl has four phenyl groups attached, and there are no surface groups at the distal ends of the dendrons. In addition, we compare the physical, optoelectronic, and device properties of **6** with first-generation dendrimers

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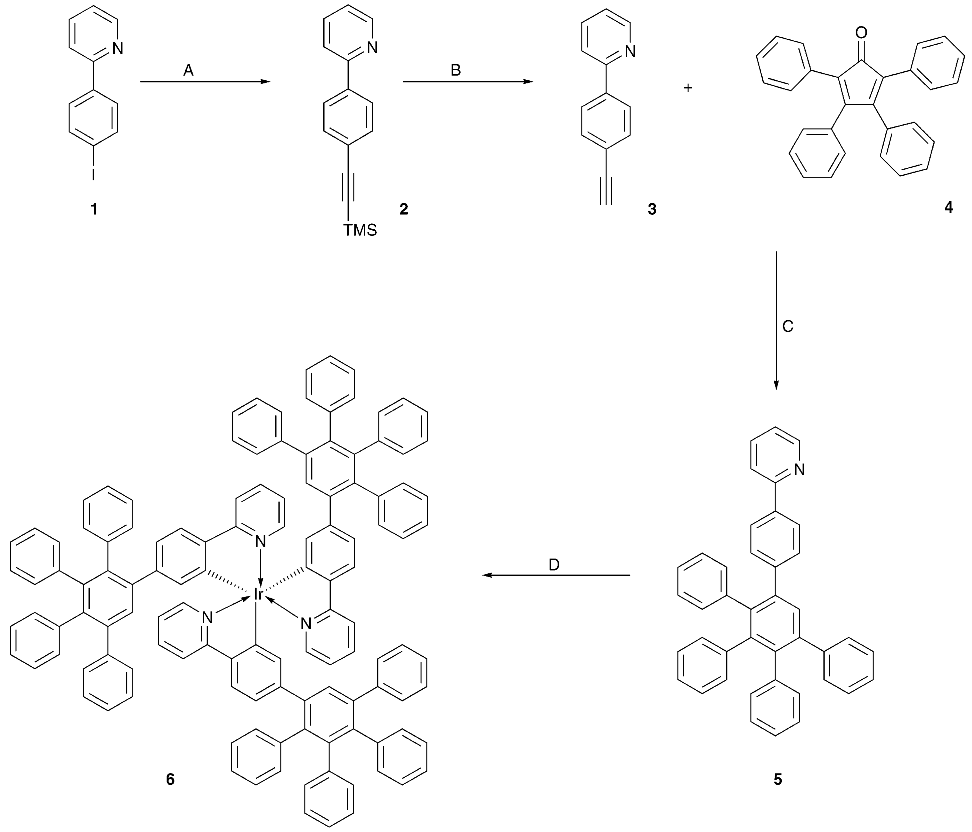
Scheme 1[a]



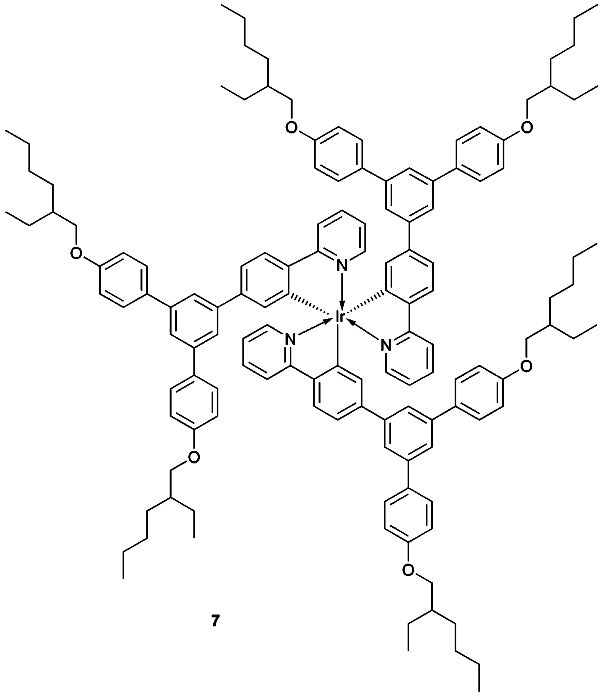
[a] Key: (A) CuI, Et_3N, TMS−acetylene, tetrakis(triphenylphosphine)palladium(0), rt, 40 h, Ar; (B) TBAF, tetrahydrofuran, rt, 3 h, Ar; (C) diphenyl ether, 210 °C, 3 h, Ar; (D) $IrCl_3 \cdot 3H_2O$, water, 2-ethoxyethanol, Δ, 16 h, Ar then **5**, silver trifluoromethylsulfonate, diglyme, 130 °C, 2 d, Ar.

7 and **8** (Figure 1). The latter two dendrimers have the same core and branching phenyl unit as in **6**, but there are only two phenyl groups attached to the branching phenyl ring. **7** and **8** also have 2-ethylhexyloxy surface groups attached to the distal ends of the dendrons.[14]

Results and Discussion

Synthesis. The strategy for the convergent synthesis of the highly branched first-generation dendrimer is shown in Scheme 1. 2-(4-Iodophenyl)pyridine (**1**) was prepared in a 40% yield by reaction of the monolithiated 1,4-diiodobenzene with 2-fluoropyridine. Trimethylsilylacetylene was then coupled with **1** under Sonogashira conditions to afford 2-(4-trimethylsilylethynylphenyl)pyridine (**2**) in an 89% yield. The acetylene was easily deprotected with either tetra-*n*-butylammonium fluoride in tetrahydrofuran or by treatment with aqueous potassium hydroxide in a methanol/dichloromethane mixture. Both methods gave 2-(4-acetylenylphenyl)pyridine (**3**) in an isolated yield of 80%. The dendronized ligand **5** was then formed by reaction of **3** with 2,3,4,5-tetraphenylcyclopentadienone (**4**).[16] The reaction was heated at 210 °C for 2−3 h using diphenyl ether as the solvent, after which **5** was isolated in a 93% yield. The complexation of **5** to form the *fac*-tris(2-phenylpyridyl)iridium(III)-cored dendrimer utilized the standard two-step procedure.[17] In the first step 2.5 equiv of **5** was reacted with iridium trichloride trihydrate in aqueous 2-ethoxyethanol heated at reflux to give a mixture of the bis(iridium), bis(chloro) dimer and unreacted ligand. This mixture was then reacted with an excess of **5** in the presence of silver trifluoromethylsulfonate in diglyme at 130 °C to give, after purification, the desired dendrimer **6** in a 63% yield for the two steps. Gel permeation chromatography (GPC) showed that the dendrimer was monodisperse, and the *facial* nature of the dendrimer was confirmed by ^{1}H NMR by comparison with spectra reported for other dendrimers with *fac*-tris(2-phenylpyridyl)iridium(III) cores.[14]

Physical Properties. The main comparison of the physical, optoelectronic, and device properties is between dendrimers **6** and **7** as they have the dendrons attached at the same point of the ligand and hence are structurally the most similar. The first difference in the physical properties between **6** and **7** was that **7** had much greater solubility in polar aprotic solvents. While **7** could be spin-coated to form good quality thin films either neat or as a blend with a host such as 4,4′-bis(*N*-carbazolyl)biphenyl (CBP), neat films of **6** tended to be much thinner and poorer quality due to the low solution concentrations associated with its much poorer solubility. This clearly demonstrates the importance of surface groups for solution processing dendrimers. The hydrodynamic radius of **6** was determined by GPC from the $\bar{M}_v$ in combination with Hester−Mitchell equation and the Mark−Houwink relationship.[18] The $\bar{M}_v$ of **6** was 954, and this corresponds to a hydrodynamic radius of 6.2 Å. The hydrodynamic radius of **6** is ≈25% smaller than the value of 8.6 Å for **7** with the difference being mainly due to the large bulky 2-ethylhexyloxy groups on **7**.[14] Nevertheless, the degree of branching in **6** is higher closer to the core, and it might be considered that the extra steric encumbrance near the core could still provide good control over the intermolecular interactions. Thermal gravimetric analysis of **6** was carried out at a scan rate of 10 °C/min under nitrogen, and the



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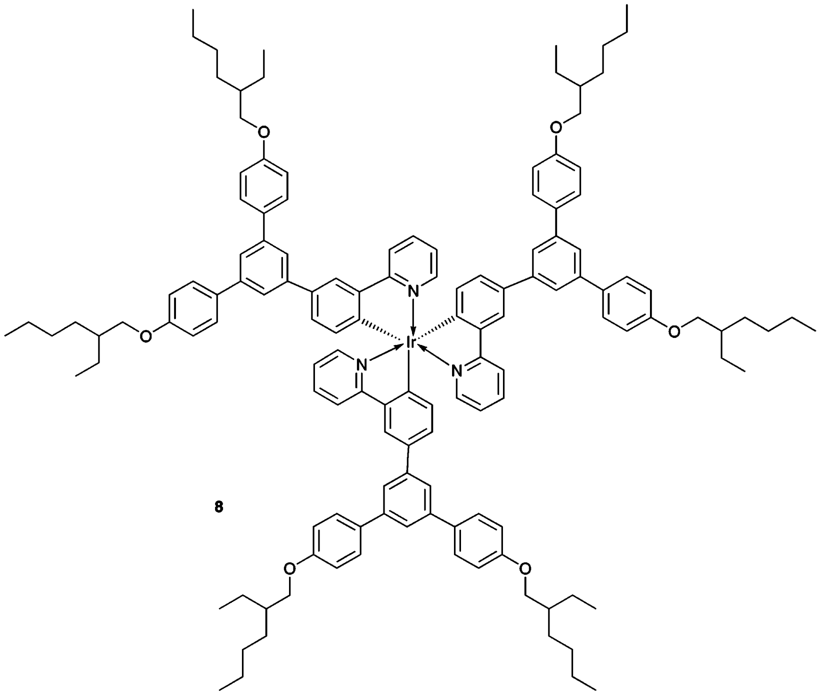

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Figure 1. Structures of **7** and **8**.

Table 1. Summary of the Thermal, Photophysical, and Electrochemical Properties of 6−8

dendrimer	$T_{5\%}$ (°C)[a]	solution[b] PLQY (%)	film PLQY (%)	$E_{1/2}$ (V) (oxidation)	$E_{1/2}$ (V) (reductions)
6	450	69	11	0.21	−2.83, −3.01, −3.18
7	400[14]	74[14]	24[14]	0.27[14]	—[c,14]
8	400[14]	70[14]	22[9]	0.24[14]	−2.91, −3.10, −3.28[14]

[a] The temperature at which 5% weight loss was observed. [b] Toluene. [c] Chemically reversible reductions were not observed.

thermal properties of the dendrimers are summarized in Table 1. For **6** there was no appreciable decomposition below 400 °C. At 450 °C there was only a 5% weight loss observed with significant decomposition occurring above this temperature. This compares favorably with the thermal properties of **7** and **8**, which both had no significant weight loss below 300 °C and only a 5% loss by 400 °C.[14] While **7** and **8** had glass transition temperatures of 138 and 132 °C, respectively,[14] **6** did not have an observable glass transition temperature.

Photophysical Properties. The addition of substituents to the ligand of *fac*-tris(2-phenylpyridyl)iridium-

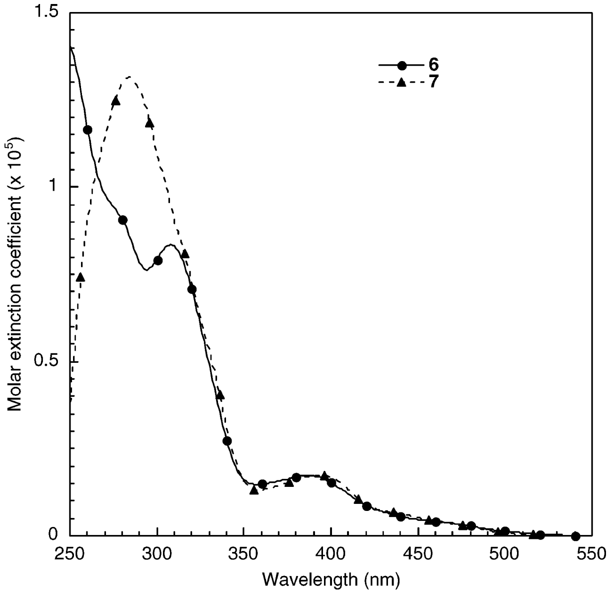

Figure 2. Solution UV−vis absorption spectra of **6** and **7** in tetrahydrofuran.

(III) complexes can change the optical properties of the complex.[19,20] For example, if the dendrons on **7** are moved from being *para* to the pyridyl ring to *meta* as in **8** (Figure 1), then the peaks and shoulders in the UV−vis absorption spectrum are blue-shifted by about 20 nm.[14] The 20 nm blue shift in the absorption spectrum of **8** is also reflected in the photoluminescence spectra. The reason for the difference in the absorption and PL spectra between **8** and **7** is that in **7** the first phenyl ring of the dendron is in conjugation with the pyridyl ring, and hence the ligand, which is responsible for the metal-to-ligand charge-transfer (MLCT) transitions with the iridium(III), has a smaller HOMO−LUMO energy gap. The solution UV−vis spectra of **6** and **7** are shown in Figure 2. The weaker long wavelength absorptions of both **6** and **7** are due to the MLCT states, whereas the stronger shorter wavelength absorptions between 260 and 350 nm are due to the ligand $\pi-\pi^*$ transitions and the dendron absorptions.[14] However, the key point from the absorption spectra is that the wavelengths of the absorptions due to the MLCT transitions of **6** and **7** are the same. While the extinction coefficients of the absorptions due to the MLCT transitions might be expected to be similar, dendrimer **6** has more than two dendron phenyl rings that can be in conjugation with the 2-phenylpyridyl ligands whereas **7** only has one. This should mean that the ligand chromophore has a longer conjugation length and hence lower HOMO−LUMO energy gap, which in turn would lead to red-shifted MLCT absorptions. The reason why the absorptions of the MLCT states of **6** are not shifted to longer wavelengths is due to the *ortho* arrangement of the "biphenyl" bonds, which causes the phenyl rings to be twisted out of plane, reducing the π-orbital overlap and delocalization pathway.

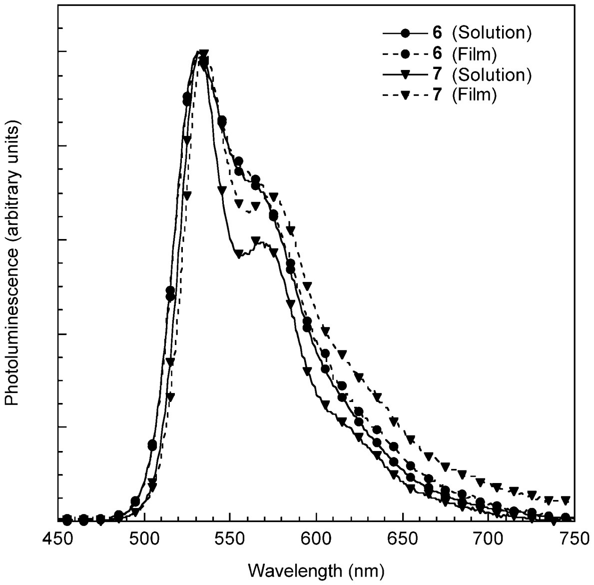

Figure 3. Solution and film photoluminescence spectra of **6** and **7**. The solutions (in tetrahydrofuran) were excited at 360 nm and the films at 325 nm. The spectra have been normalized for clarity.

The solution and film photoluminescence (PL) spectra are shown in Figure 3. In solution the PL peak maxima are the same for **6** and **7**, consistent with the absorption spectra. In moving from solution to the solid state there was no change in the PL spectrum for **6**. This is in contrast to the first-generation dendrimers **7** and **8** where a difference in the PL spectrum is seen in moving from solution to the solid state. For **8** there was a red shift of the emission peak of about 15 nm in moving to the solid state while for **7** the red shift was only around 4 nm, indicating that the attachment point of the dendrons, whether *meta* or *para* to the pyridyl ring, was important in controlling intermolecular interactions of the cores.[14] The fact that there is no change in the PL spectrum for **6** in going from solution to the solid state suggests that intermolecular interactions that lead to quenching of the luminescence might be controlled. We probed the intermolecular interactions of the emissive cores by measuring the PL quantum yields (PLQYs) with the results summarized in Table 1. The PLQY of a material is particularly sensitive to interactions of the emissive species, and if there are strong interactions of the emissive chromophores in the solid state, then the PLQY is generally observed to drop. The PLQY of **6**, **7**, and **8** in solution were 69%, 70%,[14] and 69%,[14] respectively, with the similarity showing that the attachment of the Müllen-type dendrons to the *fac*-tris(phenylpyridyl)iridium(III) core does not have a detrimental effect on the efficiency of emission. However, there is a dramatic difference in the PLQYs when moving to the solid state. For **7** and **8** the PLQY in the solid state dropped to around 22−24%,[14] while for **6** with the Müllen dendrons the PLQY was half this at 11%. This indicates that the surface groups in **7** and **8** play a very important role in controlling the intermolecular interactions in addition to the branching in the dendrons. Interestingly, when the dendrimers are blended with CBP, there is also a distinct difference between **6** and the other two materials. For **7** and **8** as 20 wt % blends in CBP the PLQYs, at 68% and 78%, were as high as the solution PLQYs. This indicates that the dendrimers were evenly distributed throughout the blended film. In contrast, the PLQY of the blended 20 wt % film of **6** in CBP had a PLQY of only 49%, which is significantly less than the solution PLQY. The lower PLQY in the blend compared to the solution measurement indicates that dendrimer **6** is not evenly distributed within the film. It should be noted that at the concentration of **6** in solution required to give neat films of thickness of order 50−60 nm the solutions were not clear and the films formed were hazy. In contrast, the blended films were mostly clear. The PLQY results further illustrate the important role the surface groups of the dendrimers play in controlling film morphology and quality. A final aspect of the photophysical study was to determine whether energy transfer from the dendrons to the core of **6** was efficient. No emission was observed from the dendron, and the photoluminescence excitation spectrum followed the absorption spectrum, showing that in common with other first-generation dendrimers energy transfer was efficient.[14,21]

Electrochemical and Device Properties. To understand where charge would be injected into dendrimer **6** in a device, we studied its electronic properties using electrochemistry with the results summarized in Table 1. The oxidation cyclic voltammagrams of **6** and **7** and reduction cyclic voltammagram of **6** are shown in Figure 4. Both **6** and **7** show a single chemically reversible oxidation corresponding to the oxidation of the core. The oxidations occur at 0.21 and 0.27 V for **6** and **7**, respectively. For **6** three chemically reversible reductions were seen at -2.83, -3.01, and -3.18 V. The oxidation of **6** occurred at a less positive potential and reductions at slightly less negative potentials than **8** (Table 1), which is consistent with **8** giving green emission and **6** green-yellow emitted light.[14]

Finally, simple single-layer devices with the dendrimer containing film directly deposited onto the indium-tin oxide (ITO) anode were prepared [ITO/20 wt % of **6**:CBP/Ca/Al], and the device characteristics are shown in Figure 5. Devices with neat films of **6** could not be prepared as the films were too thin due to its low solubility in the processing solvent. The single-layer devices showed reasonable performance. The turn-on voltage (1 cd/m^2) was 7.6 V, and the maximum external quantum was 2.9% (9.3 cd/A), with a power efficiency of 1.9 lm/W, at a brightness of 1545 cd/m^2 and 15.6 V. The fact that the highest efficiency occurs at a high drive voltage suggests that there is an imbalance of charge in the device. Previous reports on devices utilizing **7** and **8** in CBP as the emissive layers have shown electron injection and transport is one of the factors limiting device performance. The single-layer device performance observed from the blend of **6** with CBP was similar to that of **8** in the same device configuration. For the devices containing **6** 100 cd/m^2 was achieved at 11.4 V with an external quantum efficiency of 1.7% (5.4 cd/A), while for devices with **8** 100 cd/m^2 was observed at 8.8 V with an external quantum efficiency of 3.3% (11.3 cd/A).[10]

Conclusion. We have developed a simple synthetic pathway to phosphorescent dendrimers comprised of *fac*-tris(2-phenylpyridy)iridium(III) cores and highly branched “Müllen” dendrons. Although the first-generation dendrimer has a high level of branching close to the emissive core, it was not sufficient to control the intermolecular interactions in the solid state. By comparing it with dendrimers (**7** and **8**) with the same core and branching unit, fewer branches, and surface groups, it was found that surface groups play an important role in controlling both solubility and intermolecular interactions in conjugated dendrimers.

Experimental Section

Measurements. NMR spectra were recorded on Bruker DPX 400 and AV 400 MHz spectrometers: sp = surface phenyl; bp = branch phenyl; L PhH = ligand phenyl H; PyH = pyridyl H. All J values are in hertz. UV−vis spectra were recorded on a Perkin-Elmer UV−vis Lambda 14 or 25 spectrometers and were recorded as solutions in spectroscopic grade dichloromethane or dry tetrahydrofuran. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. Mass spectra were recorded on a Fisons Platform for ESI, a Micromass TofSpec 2E for matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) from dithranol (DITH) 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 ($\bar{M}_p = 580-3.2 \times 10^6$) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed with helium and pumped with a rate of 1 mL/min at 30.0 °C. Thermal gravimetric analysis was performed on a

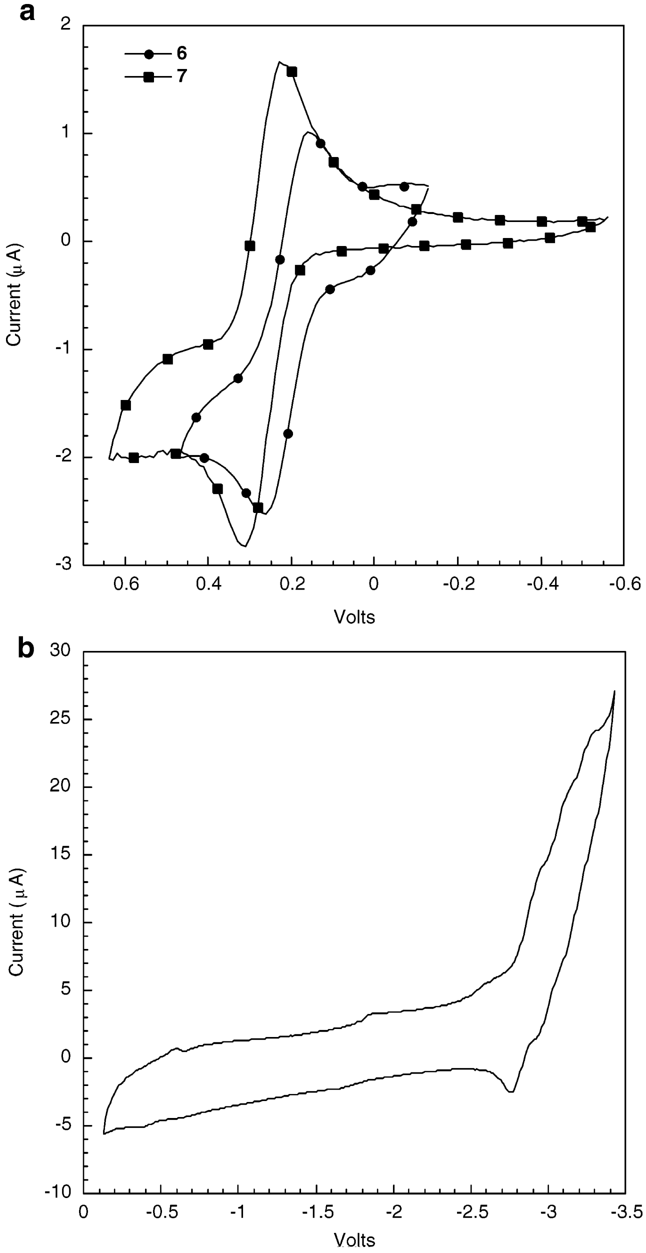

Figure 4. (a) Oxidation cyclic voltammograms of **6** and **7**. Scan rate = 30 and 40 mV/s, respectively, solvent = tetrahydrofuran for **6** and dichloromethane for **7**, concentration = 0.05 mM for **6** and 1 mM for **7**, glassy carbon and platinum working electrodes for **6** and **7**, respectively. (b) Reduction cyclic voltammogram of **6**. Scan rate = 30 mV/s, solvent = tetrahydrofuran, concentration = 0.05 mM, glassy carbon working electrode.

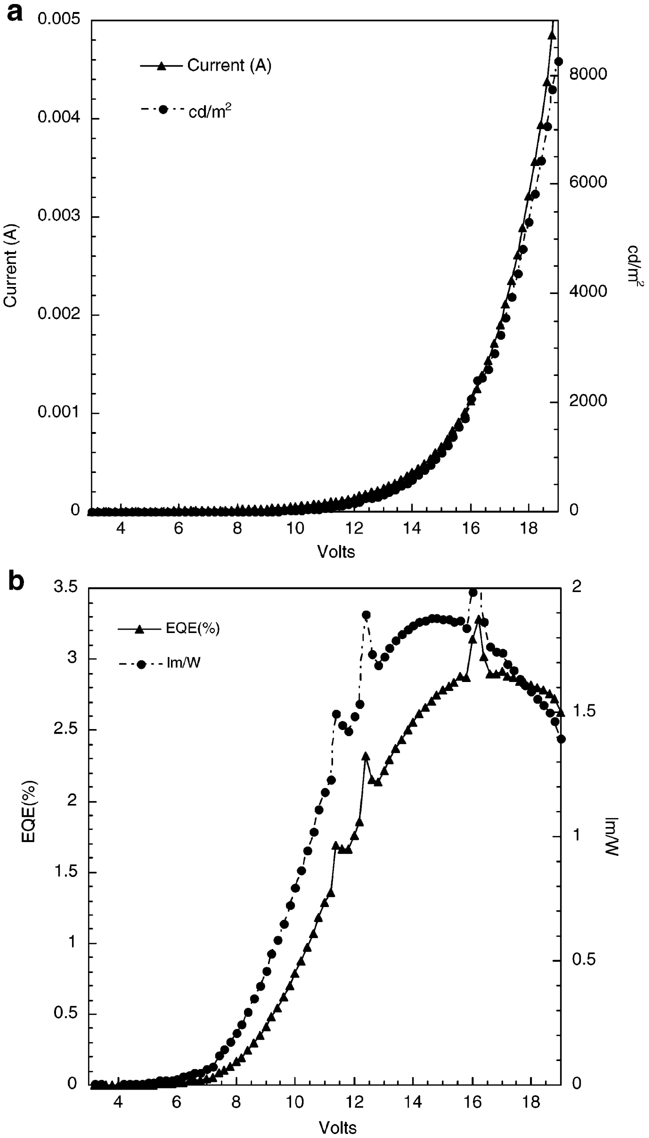

Figure 5. Device characteristics of a single-layer device (ITO/**6**:CBP 20 wt %/Ca/Al): (a) current−voltage and luminance−voltage; (b) external quantum efficiency−voltage and power efficiency−voltage.

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 passed through a column of alumina and then distilled from lithium aluminum hydride under argon. HPLC grade dichloromethane or tetrahydrofuran were used for the oxidation studies. The electrolyte was purified by recrystallization from ethyl acetate. The solutions were deoxygenated with argon. A glassy carbon working electrode, platinum wire counter electrode, and Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode was used. The ferricenium/ferrocene couple was used as standard,[22] and the ferrocene was purified by sublimation. 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 0.546 as the standard.[23] 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 ±10%.

Neat films of **6** were spin-coated from chloroform solutions with a dendrimer concentration of 10 mg/mL at 800−1200 rpm for 1 min to give a thickness of about 50−60 nm. Blend films were spin-coated from solutions of total solute concentration of 20 mg/mL at 800 rpm for 1 min to give films of thickness ≈150 nm. The PLQY of the films was measured using an integrating sphere in accordance with Greenham et al.[24] using a helium cadmium laser (Kimmon) as the excitation source. The excitation power was 0.2 mW at 325 nm, and the sphere was purged with nitrogen.

DLEDs were fabricated by spin-coating a chloroform solution of dendrimer and CBP (20:80 weight ratio) onto cleaned ITO-coated glass substrates. The ITO coated glass substrates were cleaned by ultrasound in acetone and propan-2-ol, followed by treatment with an oxygen plasma. The concentration of the dendrimer/CBP solution was around 20 mg/mL, and films were spin-coated for 1 min at a speed of 1500 rpm. The resulting thickness of the organic layer was ≈180 nm. The devices were then completed by deposition at a pressure of 10^{-6} mbar of a 30 nm layer of calcium followed by a 100 nm layer of aluminum. Current−voltage−brightness measurements were performed using a Keithley 2400 source meter and Keithley 2000 multimeter with a calibrated Si photodiode (303−674 of RS) to collect the forward emission, and efficiencies were deduced assuming Lambertian emission from the device.[25] EL spectra were recorded with a charge-coupled device (CCD) spectrograph.

2-(4-Iodophenyl)pyridine (1). A solution of 1,4-diiodobenzene (46.8 g, 142 mmol) in dry ether (450 mL) under argon was cooled in a salt−ice bath. *n*-Butyllithium (2.0 M in pentane, 72 mL, 142 mmol) was added, and the solution was stirred for 10 min. 2-Fluoropyridine (13 mL, 150 mmol) was added, and the reaction was allowed to warm to room temperature over 2 h. Water (500 mL) was added, and the organic layer was separated. The aqueous layer was extracted with ether (3 × 200 mL). The combined organic layers were washed with brine (1000 mL), dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed. The residue was purified in two steps: first by column chromatography over silica using a dichloromethane/light petroleum mixture (1:1) followed by recrystallization of the main fraction from a dichloromethane/light petroleum mixture to give **1** (17.0 g, 40%); mp 86−87 °C. Anal. Calcd for $C_{11}H_8NI$: C, 47.0; H, 2.9; N, 5.0. Found: C, 47.15; H, 2.8; N, 5.0. $\lambda_{max}(CH_2Cl_2)$/nm 262 (log ϵ/dm^3 mol^{-1}cm^{-1} 4.24), 284 (4.31). δ_H (400.2 MHz; $CDCl_3$): 7.27 (1 H, m, PyH), 7.70−7.85 (6 H, m, PyH and PhH), 8.70 (1 H, d, *J* 5 Hz, PyH). δ_C (100.6 MHz; $CDCl_3$): 95.3, 120.3, 122.5, 128.6, 136.9, 137.8, 138.8, 149.7, 156.3. *m/z* (APCI) 281.7 (MH^+, 100%).

2-(4-Trimethylsilylethynylphenyl)pyridine (2). Trimethylsilylacetylene (4.1 mL, 28.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (832 mg, 0.72 mmol) were added to a suspension of **1** (4.06 g, 14.4 mmol) and copper(I) iodide (274 mg, 1.44 mmol) in triethylamine (120 mL) that had been deoxygenated with argon. The mixture was deoxygenated with argon and then stirred under argon at room temperature for 40 h. Aqueous hydrochloric acid (3 M, 320 mL) and dichloromethane (250 mL) were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with aqueous hydrochloric acid (3 M, 30 mL), water (250 mL), and brine (250 mL), dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by column chromatography over silica using a dichloromethane/light petroleum mixture

(1:4) as the eluent. The main band was isolated and the solvent completely removed to give **2** (2.59 g, 72%); mp 56−58 °C. Anal. Calcd for $C_{16}H_{17}NSi$: C, 76.4; H, 6.8; N, 5.6. Found: C, 76.5; H, 6.8; N, 5.6. $\lambda_{max}(CH_2Cl_2)$/nm 272 sh, (log ϵ/dm^3 mol^{-1} cm^{-1} 4.67) and 294 (4.90). δ_H (400.2 MHz; $CDCl_3$): 0.27 (9 H, s, $SiMe_3$), 7.25 (1 H, m, PyH), 7.58 and 7.96 (4 H, AA′BB′, PhH), 7.73 (2 H, m, PyH), and 8.70 (1 H, m, PyH). δ_C (100.6 MHz; $CDCl_3$): −0.1, 95.5, 104.9, 120.6, 122.4, 123.7, 126.6, 132.3, 136.8, 139.2, 149.7, and 156.5. *m/z* (ESI$^+$) 252 (MH$^+$, 100%).

2-(4-Ethynylphenyl)pyridine (3). Tetrabutylammonium fluoride (1 M in tetrahydrofuran, 36 mL, 36 mmol) was added to a solution of **2** (2.26 g, 8.97 mmol) in tetrahydrofuran (50 mL), and the solution was stirred at room temperature under argon for 3 h. Dichloromethane (100 mL) and water (150 mL) were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed. The residue was purified by passing through a silica plug using dichloromethane as eluent to give **3** (1.44 g, 90%); mp 53 °C. Anal. Calcd for $C_{13}H_9N$: C, 87.1; H, 5.1; N, 7.8. Found: C, 86.7; H, 5.5; N, 7.7. ν_{max}(Nujol)/cm^{-1} 2098 (C≡C). $\lambda_{max}(CH_2Cl_2)$/nm 306 sh, (log ϵ/dm^3 mol^{-1} cm^{-1} 4.05) and 289 (4.48), 257 (4.48); δ_H(400.2 MHz; $CDCl_3$): 3.17 (1 H, s, C≡C−H), 7.26 (1 H, m, PyH), 7.61 and 7.98 (4 H, AA′BB′, PhH), 7.72−7.80 (2 H, m, PyH), and 8.71 (1 H, m, PyH); δ_C(100.6 MHz; $CDCl_3$): 78.3, 83.5, 120.6, 122.5, 122.6, 126.7, 132.5, 136.8, 139.5, 149.7, and 156.4. *m/z* (ESI$^+$) 179.8 (MH$^+$, 55%).

2-[4-(2,3,4,5-Tetraphenylphenyl)phenyl]pyridine (5). A solution of 2,3,4,5-tetraphenylcyclopentadienone (**4**)[16] (1.14 g, 2.96 mmol) and **3** (354 mg, 1.98 mmol) in diphenyl ether (3 mL) was deoxygenated and heated at 210 °C under argon for 3 h. The reaction mixture was purified by column chromatography over silica using a dichloromethane/light petroleum mixture (1:1) as eluent to give **5** (988 mg, 93%); mp 207−208 °C. Anal. Calcd for $C_{41}H_{29}N$: C, 91.9; H, 5.45; N, 2.6. Found: C, 91.5; H, 5.4; N, 2.6. $\lambda_{max}(CH_2Cl_2)$/nm 283 (log ϵ/dm^3 mol^{-1} cm^{-1} 4.38) and 259 (4.44); δ_H(400.2 MHz; $CDCl_3$): 6.80 (2 H, m, sp H), 6.85−6.96 (13 H, m, sp H), 7.15−7.24 (6 H, sp H and PyH), 7.29 and 7.83 (2 H, AA′BB′, L PhH), 7.63 (1 H, s, G1-bp H), 7.68−7.77 (2 H, m, PyH), and 8.67 (1 H, d, $J = 4.5$, PyH). δ_C (100.6 MHz; $CDCl_3$): 120.5, 122.0, 125.3, 125.6, 125.7, 126.2, 126.3, 126.4, 126.9, 127.1, 127.6, 129.9, 130.4, 131.35, 131.45, 131.5, 136.7, 137.1, 139.3, 139.5, 139.8, 139.9, 140.2, 140.25, 140.8, 141.6, 141.9, 142.5, 149.6, 157.1. *m/z* (ESI$^+$): 536.1 (MH$^+$, 100%).

***fac*-Tris[2-{4-[(2,3,4,5-tetraphenyl)phenyl]phenyl}-pyridinato-*N*,*C*$^{2'}$]iridium(III) (6).** A mixture of **5** (1.00 g, 1.87 mmol), iridium trichloride trihydrate (263 mg, 0.747 mmol), water (8 mL), and 2-ethoxyethanol (25 mL) was deoxygenated and then heated at reflux with stirring under argon for 16 h. The reaction mixture was filtered, and the residue was washed with water (3 × 50 mL). The residue was collected and dissolved in dichloromethane (200 mL), washed with water (3 × 100 mL) and brine (100 mL), dried over anhydrous magnesium sulfate, and filtered, and then the solvent was completely removed to leave a yellow solid (1.19 g) containing a mixture of bis(iridium), bis(chloro) dimer and unreacted **5**. The mixture, **5** (1.32 g, 2.46 mmol), and silver trifluoromethylsulfonate (190 mg, 0.74 mmol) in diglyme (4 mL) was heated at 130 °C under argon for 2 days. The diglyme was removed, and the crude product was purified by column chromatography over silica using a dichloromethane/light petroleum mixture (1:1) as eluent. The yellow band was collected, and the solvent was completely removed to give a bright yellow solid (1.05 g). The residue was dissolved in dichloromethane and precipitated into methanol to give **6** (841 mg, 63%); mp 274 °C. Anal. Calcd for $C_{123}H_{84}IrN_3$: C, 82.25; H, 4.7; N, 2.3. Found: C, 82.05; H, 4.7; N, 2.3. $\lambda_{max}(CH_2Cl_2)$/nm 275 sh (log ϵ/dm^3 mol^{-1} cm^{-1} 4.97), 308 (4.92), 388 (4.23) and 467sh (3.58); δ_H (400.2 MHz; $CDCl_3$): 6.32 (3 H, bt, *J* 7, sp H), 6.43−6.62 (12 H, m, L PhH, and sp H), 6.65−6.77 (12 H, m, Py H, L PhH and/or sp H), 6.77−6.95 (27 H, m, L PhH and/or sp H), 7.08 (15, bs, sp H), 7.20 (3 H, d, *J* 8, Py H), 7.28−7.34 (6 H, m, G1-bp H, L PhH), 7.52 (3 H, t, *J* 8, Py H), 7.71 (3 H, d, *J* 8, Py H). *m/z* [MALDI: DITH] Anal. Calcd for $C_{123}H_{84}IrN_3$: 1793.6 (37%), 1794.6 (51%), 1795.6 (96%), 1796.6 (100%), 1797.6 (65%), 1798.6 (28%), 1799.6 (9%). Found: 1793.2 (38%), 1794.1 (48%), 1795.1 (92%), 1796.1 (100%), 1797.2 (62%), 1798.2 (40%), 1799.3 (13%); GPC: $\bar{M}_w = 970$ and $\bar{M}_v = 954$.

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