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A Divergent Synthesis of Very Large Polyphenylene Dendrimers with Iridium(III) Cores: Molecular Size Effect on the Performance of Phosphorescent Organic Light-Emitting Diodes

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Abstract: This is a first report on a novel divergent procedure to synthesize higher generation polyphenylene dendrimers with an Ir(III) core up to **G4**, which up to now is the largest Ir(III) dendrimer, having a molecular diameter of 8 nm. Our synthetic method provides a much higher yield (>80%) than earlier reported traditional convergent strategies (<35%). Moreover, with a stepwise synthesis, the molecular sizes are controlled by different dendrimer generations from **G1** ($R_1 \approx 15$ Å) to **G4** ($R_4 \approx 40$ Å). In this case, polyphenylene dendrons are used as a "matrix" which prevent iridium phosphorescent cores from triplet−triplet annihilation and improve their photoluminescence quantum yields (PLQYs). All dendrimers show strong phosphorescence at room temperature, and interestingly, their PLQYs tend to increase with subsequent generations up to 36% for **G4** in solid state, almost 4 times of that of the nondendritic iridium complex. We also fabricated all generation dendrimers in phosphorescent organic light-emitting diodes (PhOLEDs) and investigated the relationship between the Ir(III) dendrimer sizes and the device performances. Our results indicate that dendrimer **G3** possesses the highest efficiency device compared to other generation dendrimers, since its appropriate dendrimer size ($R_3 \approx 30$ Å) can not only prevent intermolecular triplet−triplet annihilation, thereby increasing the PLQY, but also provide an effective charge carrier mobility from the periphery to the Ir(III) core.

Introduction

Phosphorescent organic light emitting diodes (PhOLEDs) have entered the commercial stage and have been intensively investigated for their applications in high-efficiency, low-drive voltage, full-color, large-area flat-panel displays.[1−5] The inclusion of highly phosphorescent heavy-metal organic complexes as dopants ensures that both singlet and triplet excitations formed on charge recombination can increase the internal quantum efficiency to 100%, corresponding to an external quantum efficiency of more than 20%.[6−9] Among those, Ir(III) complexes are particularly important and have been thoroughly studied.[10−15] Due to the complication and high cost of vacuum deposition which is often used to fabricate small molecule based PhOLEDs,[10−12] solution processing offers a lower cost approach to large-area full color displays.[13−15] Nevertheless, most small phosphorescent Ir(III) complexes and their solution processable polymers have to be blended into host materials as the emitting layers in PhOLED devices.[12,16,17] The phase separation in physical blend systems inevitably deteriorates the device

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performance.[18,19] On the other hand, PhOLEDs can also be fabricated by covalent bonding of Ir(III) complexes to the polymer main chains or pendant chains.[20,21] Unfortunately, the performance of these solution-processed PhOLEDs is still significantly lower than that of their vacuum-deposited counterparts. This is caused not only by impurities in the polymers but also by the triplet energy levels ($E_T = 2.4$ eV) of Ir(III) complexes which allow for an energy transfer to the polymer chains,[12,22,23] thus decreasing their phosphorescent efficiencies.

In general, the phosphorescence of Ir(III) complexes is quite sensitive to their concentration due to the aggregation induced triplet−triplet annihilation.[10,18,24] Therefore, the most efficient devices based on Ir(III) complexes have to blend matrix materials as a host to keep the emissive chromophores separated. While the physical mixture may be well-defined, it is difficult to determine what the distribution and arrangement of the two components are in the deposited film. The dendritic architectures can overcome this weakness and combine the host−guest composition at a molecular level to control the intermolecular interactions of Ir(III) complexes by the dendrimer generations.[25−27] With a rigid scaffold, numerable chromophores can be accurately located in different positions such as the core,[27] dendrons,[28] and the outer periphery.[29] Several types of phosphorescent dendrimers have been successfully synthesized and promisingly fabricated to PhOLEDs via solution processes.[26,30]

The design and synthesis of different generation dendrimers to control their molecular sizes, and thus improve their performance in PhOLEDs, are a great challenge.[31,32] Suitable dendrimer size can not only prevent the interaction among the emissive cores but also avoid significant reduction in charge transport and recombination. However, the development of such higher-generation Ir(III) dendrimers represents a synthetic challenge due to the stability and solubility of Ir(III) complexes. The coordination between Ir(III) and the 2-phenylpyridine ligand can be destroyed by most metal-based catalysts such as nickel and copper. Stability is only preserved in palladium-catalyzed reactions such as *Suzuki* and *Stille* coupling,[33,34] resulting in a lack of efficient synthetic routes toward higher generation dendrons. Therefore, most previous Ir(III) dendrimers have been synthesized via a convergent strategy:[15,31] This route involves the preparation of the polyphenylene or polycarbazole dendronized ligands and subsequent complexation with Ir(III) salts in glycerol to give Ir(III) dendrimers. To the best of our knowledge, the third generation dendronized ligand so far reported was the largest ligand complexed with Ir(III).[30,35] However, the low yield was in the range of 10−35%. The fourth generation Ir(III) dendrimers have never been reported, since their larger dendronized ligands possess limited solubility in glycerol, resulting in incomplete complexation. In this study, we have investigated a novel divergent procedure that rapidly leads to first, second, third, and even fourth generation polyphenylene dendrimers with *fac*-tris[2-phenylpyridyl]Ir(III) as cores (**G1**, **G2**, **G3**, and **G4**, Scheme 1) in high yield (>80%). Up to now, dendrimer **G4** is the largest Ir(III) dendrimer with a radius up to 4 nm (Scheme 1, calculated by a molecular mechanics simulation).

The high generation polyphenylene dendrimers demonstrate good solubility in common solvents, such as dichloromethane, tetrahydrofuran, and toluene, and thus high solution processability in PhOLED devices. From the molecular design point of view, the combination of polyphenylene dendrons and Ir(III) complexes can form a molecule composed of an emitting Ir(III) core considered as a guest coupled with rigid dendrons as the host shell. This self-host−guest system[36] provides a new strategy for designing highly efficient, solution-processable phosphorescent materials for nondoped PhOLED devices. Recently, the first generation Ir(III) polyphenylene dendrimer via a convergent procedure has been introduced.[37,38] However, due to their low generation, the electroluminescence (EL) properties were not satisfactory. Hence, we herein report a new strategy to produce high generation polyphenylene Ir(III) dendrimers up to **G4**.

Results and Discussion

Synthesis and Structure Characterization. Regarding the straightforward strategies for the preparation of dendrimers, not only phosphorescent Ir(III) cores with high stability should be considered in the divergent synthetic route but also selective coupling reactions with a high yield should be included. Herein, the simplest *fac*-tris(2-phenylpyridyl)Ir(III) core with a high phosphorescent quantum yield[39] and a noncatalytic [4 + 2] *Diels−Alder* cycloaddition[40] were selected for constructing very large polyphenylene dendrimers. Therefore, the most important dendritic core with three ethynyl groups, i.e., *fac*-tris[2-(3-ethynylphenyl)pyridyl]Ir(III) (**3**), was synthesized as the key building block (Scheme 2). The first step involved the iodination of *fac*-tris(2-phenylpyridyl)Ir(III) (Ir(ppy)$_3$) with iodine and iodobenzene diacetate in dichloromethane[41] to obtain *fac*-tris[2-

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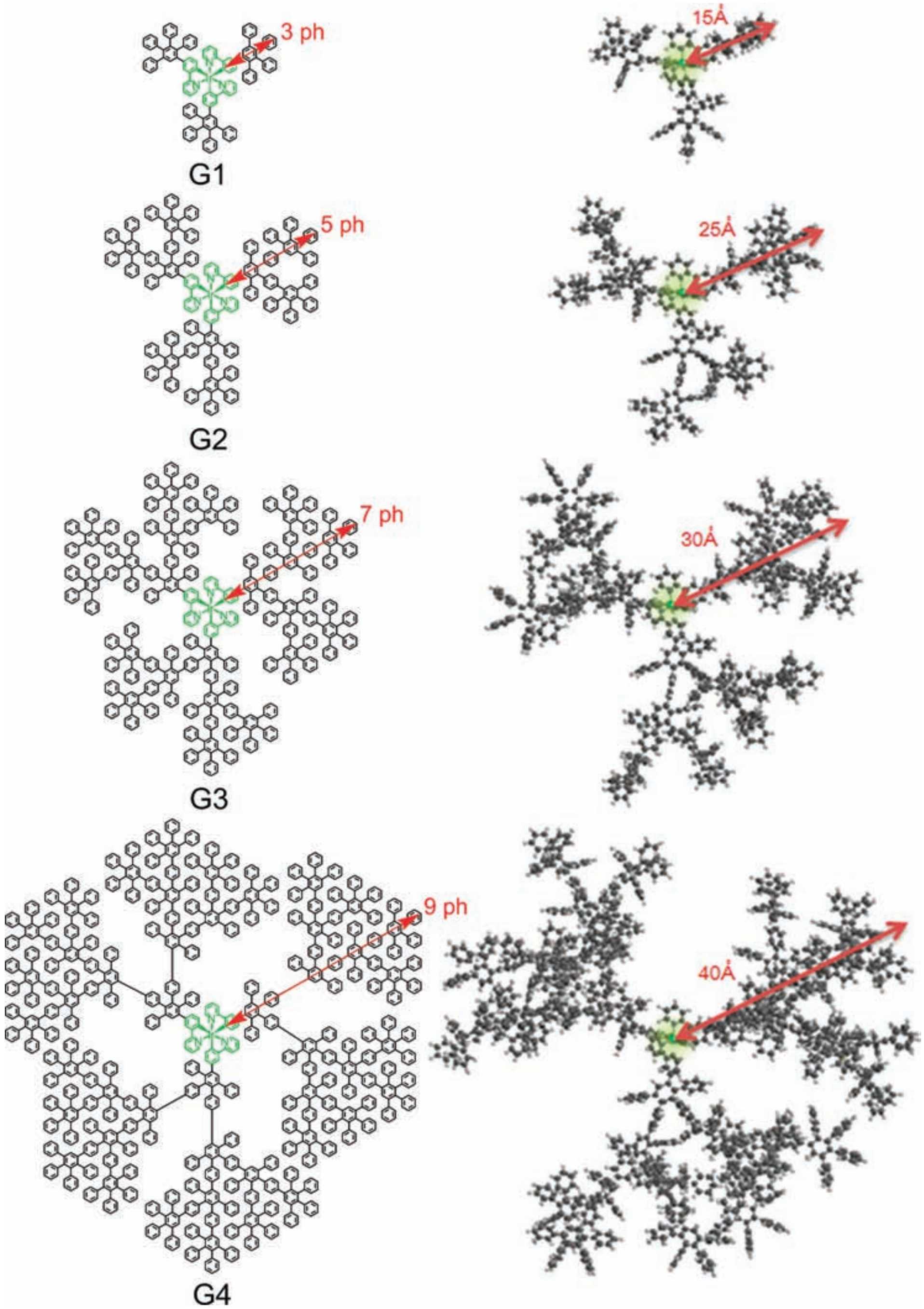
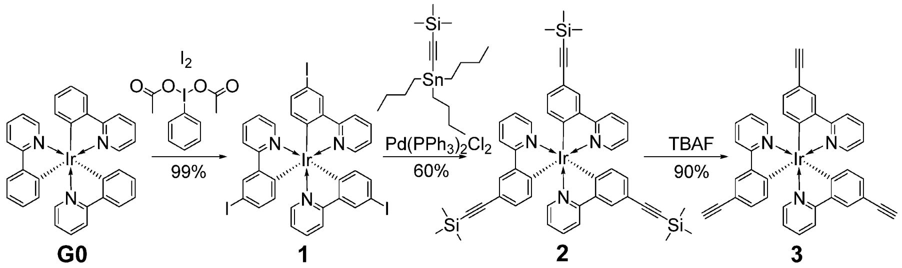
Scheme 1. Polyphenylene Dendrimers (**G1**, **G2**, **G3**, and **G4**) with an Ir(III) Core

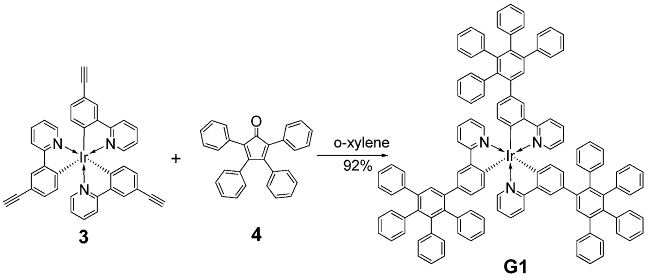


Scheme 2. Synthesis of *fac*-Tris[2-(3-ethynylphenyl)pyridyl]Ir(III) Core **3**



(3-iodophenyl)pyridyl]Ir(III) (**1**) in quantitative yield. Complex **1** was reacted with trimethyl((tributylstannyl)ethynyl)silane using dichloro-bis(triphenylphosphine)palladium(II) as the catalyst under *Stille* coupling conditions. It was found that using THF as the solvent resulted in higher yields (60%) of *fac*-tris[2-(3-((trimethylsilyl)ethynyl)phenyl)pyridyl]Ir(III) (**2**) compared

Scheme 3. Synthesis of First-Generation *fac*-Tris[2-phenylpyridyl]Ir(III) Core Polyphenylene Dendrimer (**G1**)

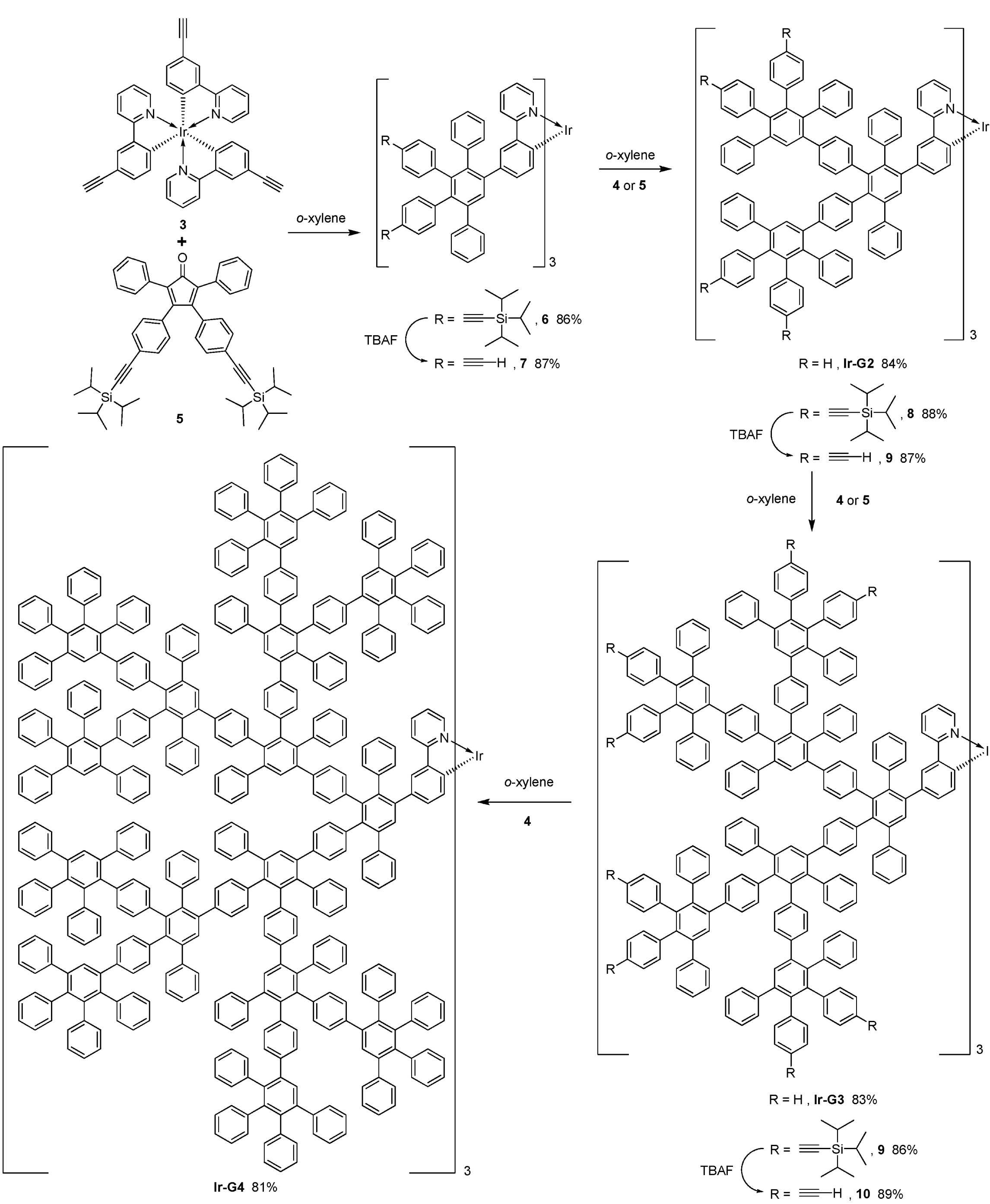


to the use of toluene as solvent (32%). Deprotection of **2** was achieved by treatment with tetrabutylammonium fluoride in THF at room temperature, and Ir(III) core **3** was isolated in 88% yield.

The first-generation dendrimer **G1** (Scheme 3), with three polyphenylene dendronized ligands, was synthesized by refluxing an *o*-xylene solution of the Ir(III) core **3** and commercially available tetraphenylcyclopentadienone (**4**) in a microwave reactor for 2 h. After GPC column separation, the first-generation dendrimer **G1** was precipitated in methanol as a yellow powder in 92% yield.

The synthesis of the higher-generation Ir(III) dendrimers was carried out following a divergent synthetic protocol.[42] By employing a [4 + 2] *Diels–Alder* cycloaddition procedure of

Scheme 4. Synthesis of Dendrimers **G2**, **G3**, and **G4**



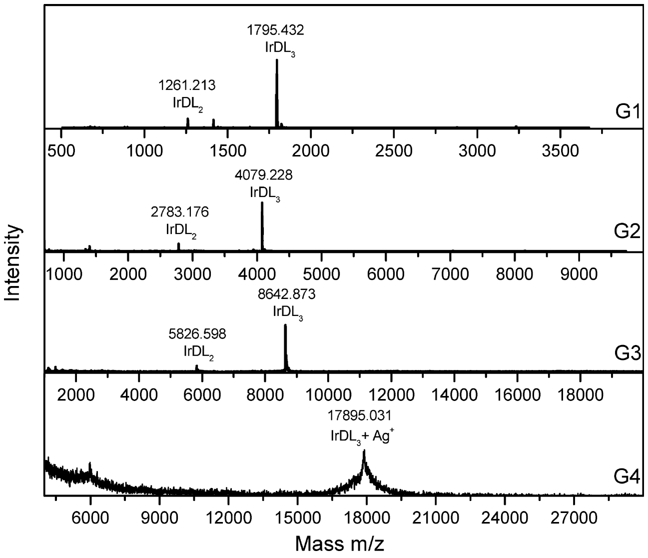


Figure 1. MALDI-Mass spectra for **G1**, **G2**, **G3**, and **G4**.

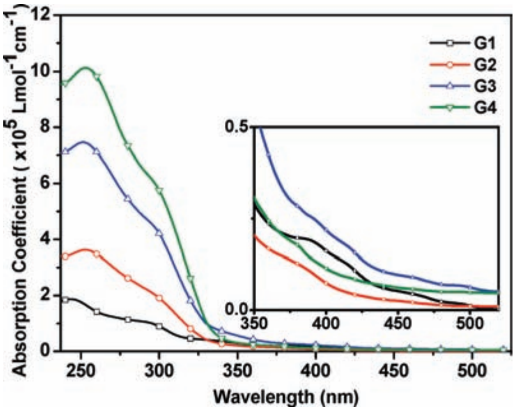


Figure 2. UV−vis absorption spectra of dendrimers in DCM solutions.

the triisopropylsilyl (TiPS) protected ethynyl-substituted cyclopentadienone branching unit **5** to the ethynyl-substituted core **3**, the first-generation dendrimer **6** (Scheme 4) with TiPS-ethynyl groups was formed in 86% yield. After the removal of the TiPS groups in **6** with tetra-*n*-butylammonium fluoride (TBAF), dendrimer **7** was achieved with "free" ethynyl groups in 87% yield. The resulting activated ethynyl groups were further treated with "end-capping" building block **4** to achieve the second-generation dendrimer **G2** (84%) or with "adaptable" building block **5**. Then this cycle of cycloaddition, deprotection, and end-capping was repeated to third and fourth generation dendrimers (**G3** and **G4**) with high yields (>80%) for all steps.

The structures of dendrimers **G1**, **G2**, **G3** and **G4** were elucidated by NMR spectroscopy and MALDI-TOF mass spectrometry. The MALDI-TOF mass spectra (Figure 1) revealed a main intense signal corresponding to the calculated mass of the four dendrimers with three dendronized ligands ($Ir(DL)_3$), and an additional signal belonging to fragments with only two dendronized ligands ($Ir(DL)_2$).

Photophysical Properties. The UV−vis absorption spectra (Figure 2) of Ir(III) dendrimers **G1**, **G2**, **G3**, and **G4** were measured in dichloromethane solutions at 298 K (Table 1). In general, the absorption spectra of lower generation dendrimers **G1** and **G2** could be divided into two components. The short wavelength regions below 300 nm were predominantly attributed to the intraligand $\pi-\pi^*$ transition of the polyphenylene dendrons, while the longer wavelength absorptions at ~350−450 nm were primarily due to the metal-to-ligand charge transfer (MLCT) state of the Ir(III) core.[43] However, for higher generation dendrimers **G3** and **G4**, the MLCT shoulders could not be clearly detected due to the intense absorption of their larger dendritic ligands.[44]

Table 1. Molecular Weights (M), Diameters of Dendrimers, Absorption (λ_{abs}) and Emission (λ_{em}) Maxima, and Solution and Film Photoluminescence Quantum Yield (Φ_P)

	M [gmol^{-1}]^a	d^b [Å]	$\lambda_{abs}{}^c$ [nm] (log ξ)	$\lambda_{em}{}^d$ [nm]	$\Phi_P{}^f$ (%)	$\lambda_{em}{}^e$ [nm]	$\Phi_P{}^e$ (%)
G1	1795.4	30	244(5.3), 294(5.0), 336(4.6), 390(4.3), 414(4.1)	516	39	527	8
G2	4079.2	50	253(5.6), 298(5.3), 384(4.1)	516	49	525	22
G3	8642.9	60	253(5.9), 298(5.6)	516	53	525	30
G4	10895.0*	80	253(6.0), 298(5.8)	516	56	516	36

[a] Measured by MALDI-TOF mass spectrometry using dithranol as matrix; * means Ag^+ cationization agent was added. [b] Calculated from MM+ simulation method. [c] Measured in CH_2Cl_2 at 298 K with a concentration of 10^{-6} M. [d] Measured in CH_2Cl_2 at 298 K with a concentration of 10^{-5} M and excitation wavelength of 380 nm. [e] The data of neat films measured at 298 K, which were prepared by drop-coating on quartz substrates. PL spectra were measured with the excitation wavelength of 409 nm. [f] Measured in N_2-saturated toluene at 298 K with $Ir(ppy)_3$ as the reference and the excitation wavelength of 390 nm.

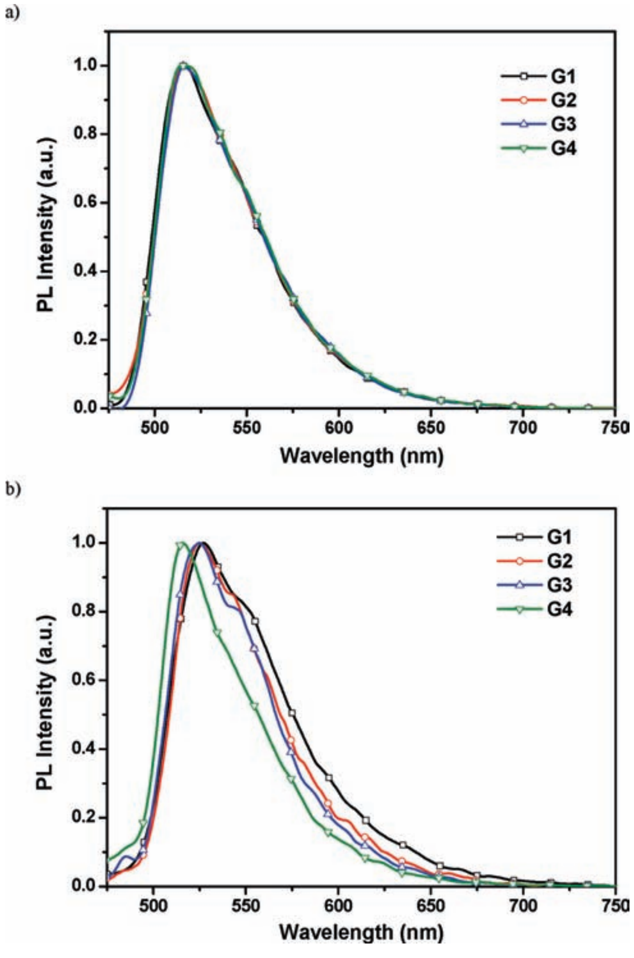


Figure 3. Photoluminescence (PL) spectra of dendrimers (a) in DCM solutions with a concentration of 10^{-5} M (λ_{ex} = 380 nm) and (b) in thin films (λ_{ex} = 409 nm).

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The photoluminescence (PL) spectra of dendrimers **G1**, **G2**, **G3**, and **G4** in dichloromethane solutions and in solid films are shown in Figure 3a and 3b. Similar to Ir(ppy)$_3$,[39] all dendrimers exhibited only one green emission peak at 516 nm. In contrast, in the solid state, the PL maximum of dendrimer **G1** showed a bathochromic shift of 11 nm compared to the dichloromethane solution, indicating that the first generation polyphenylene dendrons were not sufficient to prevent intermolecular interaction. However, with the dendrimer generation increasing from the second to the fourth, the aggregation induced bathochromic shift was reduced from 9 to 0 nm. This suggested that intermolecular interactions of the emissive cores could be effectively controlled by larger dendrons in higher generation dendrimers.

We further probed the photophysical properties of the dendrimers by measuring their PL quantum yields (PLQYs) in solutions and in solid films (Table 1) with Ir(ppy)$_3$ (40%) as the reference.[45] In N$_2$-saturated toluene solutions, dendrimer **G1** possessed nearly the same relative PLQY (39%) as Ir(ppy)$_3$; the relative PLQYs of higher generation dendrimers increased along with their growing generations, from 49% for **G2**, 53% for **G3**, to 56% for **G4**, respectively, because of their better chromophore separation. The film PLQYs were measured with an integrating sphere under an excitation wavelength of 409 nm.[46] The film of the largest dendrimer **G4** exhibited an absolute Φ_P of 36%, which was 4 times higher than that of **G1** (8%), indicating a significantly reduced quenching between Ir(III) cores.[47] Moreover, the absolute Φ_P of **G4** in film was nearly the same as the relative Φ_P of **G1** in solution, which suggested that the fourth-generation dendrons were almost completely able to suppress the self-quenching between Ir(III) cores when going from solution to film.[48]

Electrochemical Properties. To understand at which potential charges would be injected into the dendrimers in PhOLEDs, cyclic voltammetry (CV) measurements were performed to study the electrochemical properties of all dendrimers. The oxidation cyclic voltammograms of three dendrimers (**G1**, **G2**, and **G3**) are shown in Figure 4 (the oxidation of **G4** was too weak to be recognized). All three dendrimers demonstrated reversible oxidation potentials at ca. 0.63 V vs a Ag/Ag$^+$ electrode, which were assigned to the oxidation of the iridium metal cationic site (Ir(III)→Ir(IV)).[49] According to the onset potential of the oxidation process (0.63 V), the highest occupied molecular orbitals (HOMOs) of dendrimers **G1**, **G2**, and **G3** were estimated to be approximately −5.0 eV according to the formula $E_{\mathrm{HOMO}} = -(E^{\mathrm{ox}} + 4.34)$.[50] The energy levels of the lowest unoccupied molecular orbital (E_{LUMO}) of the three dendrimers were calculated to be approximately −2.6 eV by subtraction of the optical band gap (2.4 eV, taken from the onset of absorption at 516 nm, Figure 2) from the E_{HOMO}.

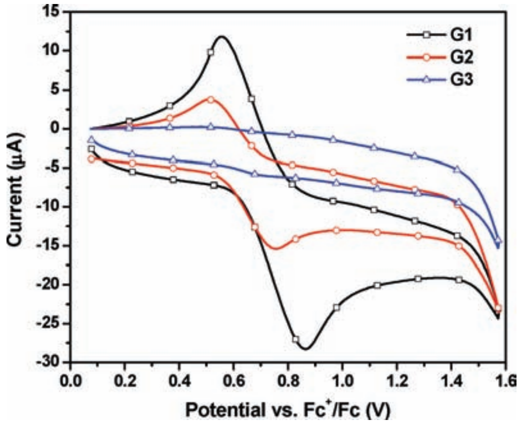

Figure 4. Cyclic voltammetry of dendrimers **G1**, **G2**, and **G3**. The voltammograms have been offset for clarity. All the oxidation potentials are quoted against the ferricenium/ferrocene couple.

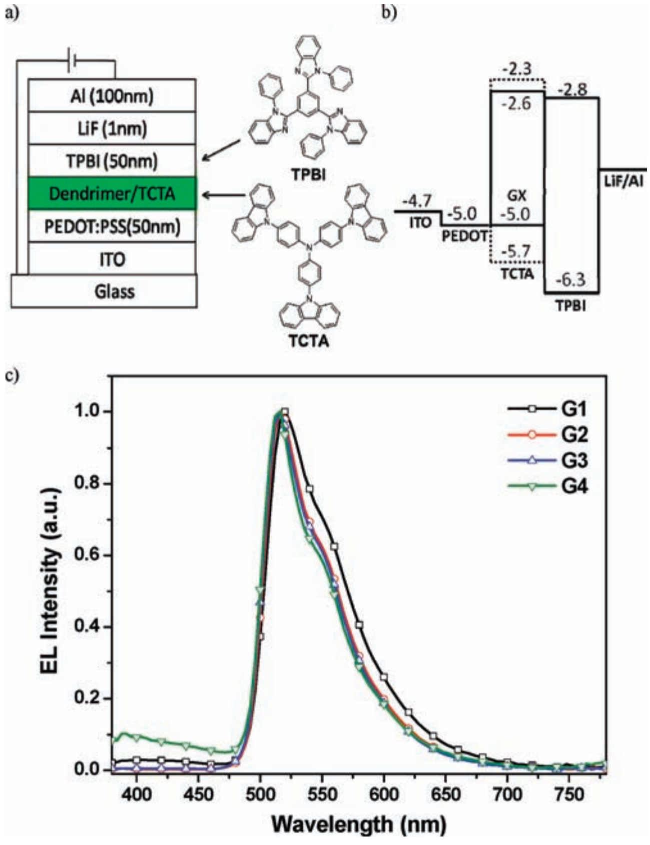

Figure 5. (a) Schematic diagram of electroluminescence (EL) device configurations, (b) energy level diagram, and c) EL spectra at driving voltage of 8 V.

Electroluminescent Properties. To test the electroluminescent properties of all dendrimers, nondoped PhOLEDs were first fabricated in a standard sandwich geometry using the following configuration: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS)/dendrimers/1,3,5-tris(2-*N*-phenylbenzimidazolyl)- benzene (TPBI)/LiF/Al (Figure 5a), leading to the energy diagram depicted in Figure 5b. TPBI was used as the electron-transporting and hole-blocking material.

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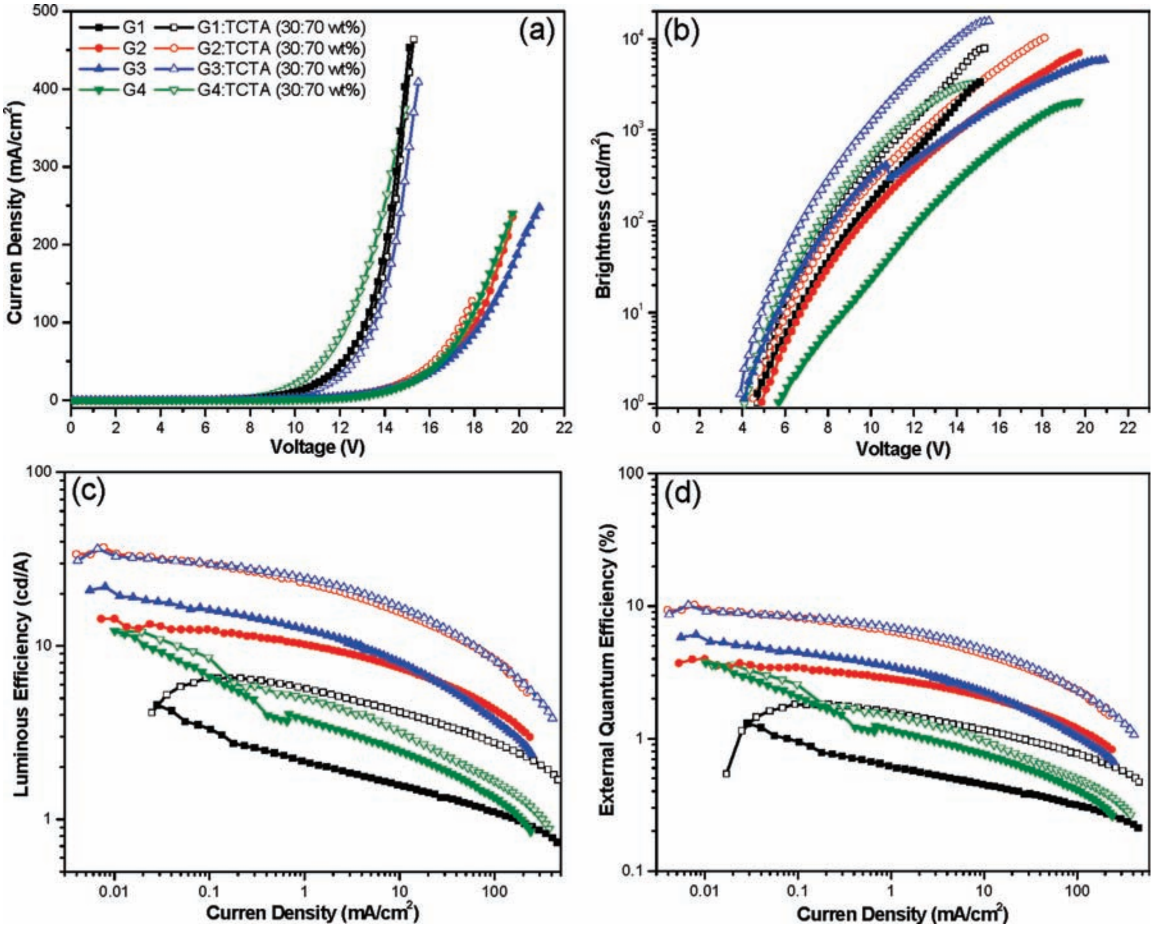

Figure 6. Characteristics of devices using dendrimers **G1**−**G4** (also blended with TCTA). (a) Current density versus voltage, (b) brightness as a function of voltage, (c) luminous efficiency versus current density, and (d) EQE as a function of current density.

Table 2. Performance of the Devices Based on the Four Dendrimers

	$\eta_{c,\ max}$ [cd/A]	$\eta_{ext,\ max}$ [%]	turn-on voltage[a] [V]	η_c[b] [cd/A]	η_{ext}[b] [%]	voltage[b] [V]	η_c[c] [cd/A]	η_{ext}[c] [%]	voltage[c] [V]	λ_{em} [nm]	CIE at 8 V (*x*, *y*)
G1	4.6	1.3	4.7	1.7	0.6	9.3	1.1	0.3	13.0	520	(0.33, 0.60)
G2	14.4	4.0	4.9	10.2	3.3	9.5	7.0	1.6	14.1	516	(0.31, 0.63)
G3	21.9	6.1	4.1	12.9	4.9	8.3	7.4	1.7	14.0	516	(0.30, 0.63)
G4	12.2	3.8	5.7	3.1	0.8	12.2	1.5	0.3	17.0	516	(0.29, 0.58)
G1 (30 wt %)	6.6	1.8	4.7	5.3	1.8	8.1	3.5	1.0	11.6	520	(0.32, 0.62)
G2 (30 wt %)	37.0	10.3	4.5	26.3	9.7	8.6	17.6	4.4	12.4	516	(0.31, 0.63)
G3 (30 wt %)	36.5	10.2	3.9	27.0	9.6	6.8	19.1	6.1	9.7	516	(0.30, 0.63)
G4 (30 wt %)	12.1	3.6	4.1	4.4	1.8	7.7	2.0	0.6	11.1	516	(0.29, 0.58)

[a] At a brightness of 1 cd/m². [b] At a brightness of 100 cd/m². [c] At a brightness of 1000 cd/m²; η_c, luminous efficiency; η_{ext}, external quantum efficiency.

The device characteristics and performance as current density and brightness versus voltage as well as luminous efficiency and extern quantum yield (EQE) versus current density are shown in Figure 6a−d and tabulated in Table 2. All dendrimers exhibited EL spectra identical to their PL counterparts (Figure 5c) with Commission International de L'Eclairege (CIE 1931) coordinates of (0.33, 0.60), (0.31, 0.63), (0.30, 0.63), and (0.29, 0.58), respectively, which indicated that all EL came from the triplet excited states of the dendrimers. Moreover, the EL spectra of all dendrimers were independent of the applied voltage varying from 6 to 16 V, which were attributed to their rigid polyphenylene frameworks. The turn-on voltage (defined as the bias at a brightness of 1 cd m^{-2}) of dendrimer **G3** (4.1 V) was slightly lower than that of the other three dendrimers (**G1**, **G2**, and **G4**). Moreover, as shown in Figure 6b−d, a maximum brightness of 3340, 7030, 5900, and 2040 cd/m², a maximum luminous efficiency of 4.6, 14.4, 21.9, and 12.2 cd/A, and a maximum EQE of 1.3, 4.0, 6.1, and 3.8% for **G1**, **G2**, **G3**, and **G4**, respectively, were observed.

To improve the device performance, the doped devices with TCTA as a host were fabricated. The best device performances were obtained with concentrations of 30% for all. However, the EQEs and luminous efficiencies of nondoped **G2** (4.0%, 14.4 cd/A) and **G3** (6.1%, 21.9 cd/A) devices were still much higher than those of the doped **G1** (1.8%, 6.5 cd/A) device with TCTA. This could be attributed to the advantages of the self-host−guest system in our dendrimers which consisted of an Ir(III) emissive core and rigid polyphenylene dendrons. Figure 6a demonstrated the nondoped and doped devices of **G1** and **G2** possessed almost identical *I*−*V* curves but the doped systems of **G3** and **G4** had higher current densities than their nondoped systems. These results indicated both polyphenylene dendrons and the host TCTA can contribute to the $I-V$ characteristics. The carrier mobility reduces with increasing dendron generation, which has been found in polyphenylene dendrimers.[51] However, the TCTA molecules could be bound into the dendritic frameworks of higher generation dendrimers to transport holes from the periphery to the Ir(III) core.[52] As shown in Figure 6c and d, the maximum EQE and brightness of doped devices were up to 10.3%, 37.0 cd/A for **G2** and 10.2%, 36.5 cd/m^2 for **G3**, respectively, which was more than 5 times higher than that of the doped **G1** device. The performances of doped devices were comparable to that of dendrimers previously reported.[15,26] However, the divergent synthesis approach will lead to further improvements in the molecular design.

Nevertheless, the performances of nondoped and doped devices of the largest Ir(III) dendrimer **G4** were suddenly reduced because of its overlarge molecular size ($R_4 \approx 40$ Å) from the outer dendrimer periphery to the Ir(III) core. As it was shown earlier for other core derivatives and extended polyphenylene dendrimers,[53] the twisted polyphenylene spacers interrupt the π-conjugation and reduce the charge carrier mobility with the number of units increasing.[54,55] Therefore, the charge injection to the core is hampered. Partial charges prefer to delocalize on the outer phenylene units, and after considerable equilibration time the charges can enter the core. This is the reason why dendrimer **G4** demonstrated the highest PLQY but a lower device performance.

Conclusions

In summary, we developed a novel divergent strategy to synthesize high generation polyphenylene dendrimers with Ir(III) cores up to **G4**, which is the largest Ir(III) dendrimer up to now and has never been synthesized by previous methods. Nevertheless, the novel divergent procedure can simplify the color tuning of Ir(III) dendrimers not only by using different homoleptic cyclometalated ligands[56] but also by importing multicolor chromophores into the core, dendrons, and shell groups in dendrimers.[57] Besides many of the desired properties achieved at an appropriate molecular size, the efficiency of simple device architectures can easily balance the effort required for their synthesis. In this paper, our four generations of Ir(III) dendrimers offer a unique opportunity to develop the relationship between the Ir(III) dendrimer sizes and their PhOLED performances. The modular molecular architecture gives tremendous scope for tuning a wide range of properties in addition to color, such as intermolecular interactions, charge mobility, and exciton diffusion. The most important issue is that our investigation of the device performances on different size dendrimers indicates the effective charge injection distance into the Ir(III) core is ~30 Å. The suitable molecular size can not only prevent intermolecular triplet−triplet annihilation, thus increasing the PLQY, but also provide an effective charge carrier mobility from the periphery of dendrimer to the Ir(III) core.

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Supporting Information Available: Detailed experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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