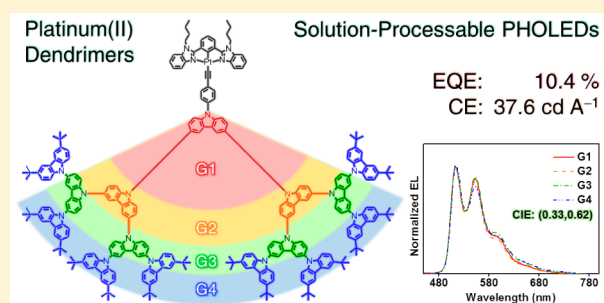


# Design Strategy for High-Performance Dendritic Carbazole-Containing Alkynylplatinum(II) Complexes and Their Application in Solution-Processable Organic Light-Emitting Devices

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**ABSTRACT:** A new class of luminescent dendritic carbazole-containing alkynylplatinum(II) complexes has been synthesized, characterized, and applied as phosphorescent dopants in the fabrication of solution-processable organic light-emitting devices (OLEDs). These complexes exhibit high photoluminescence quantum yields of up to 80% in spin-coated thin films. In addition, the incorporation of carbazole dendrons into the platinum(II) center can significantly suppress intermolecular interactions in solid-state thin films, giving rise to emission spectra that are similar to those found in solution irrespective of dopant concentrations. High-performance solution-processable OLEDs have also been fabricated, with a maximum external quantum efficiency of up to 10.4%, which is comparable to that of the vacuum-deposited devices based on the small-molecule counterpart. This is one of the highest ever reported values for solution-processable devices based on platinum(II) complexes with tridentate ligands.



## INTRODUCTION

Phosphorescent organic light-emitting devices (PHOLEDs) based on transition metal complexes as emissive dopants have received enormous attention because of their extremely high efficiencies.<sup>1</sup> The presence of a heavy metal center leads to strong spin-orbit coupling and fast intersystem crossing due to heavy atom effect, theoretically yielding 100% internal quantum efficiency.<sup>2</sup> Recently, state-of-the-art PHOLEDs prepared by vacuum deposition have been reported to demonstrate high external quantum efficiencies (EQEs) of over 30%.<sup>3</sup> However, the development of solution-processable PHOLEDs is still lagging behind,<sup>4</sup> in that their electroluminescence (EL) performances are comparatively poorer than those of the vacuum-deposited counterparts.<sup>3,4</sup> This is probably due to the limited solubility and the poor film forming ability of the complexes.<sup>4a,b</sup> Recent demonstration of the design and synthesis of phosphorescent dendrimers has opened up a new opportunity to realize high-performance solution-processable PHOLEDs.<sup>5-8</sup> Dendrimers containing different metal centers including rhenium(I),<sup>6a</sup> ruthenium(II),<sup>6b</sup> europium(III),<sup>6c</sup> platinum(II),<sup>6d-g</sup> and gold(III)<sup>8</sup> have been reported for PHOLED applications. Among these metal-containing dendrimers, iridium(III) dendrimers have generally received much attention.<sup>7</sup> For example, Wang and co-workers developed a class of green-emitting iridium(III) dendrimers with carbazole dendrons and *tert*-butyl surface groups for solution-processable PHOLED applications.<sup>7c</sup> Promising device performance was achieved with a maximum EQE of 16.6% and a current efficiency of 57.9 cd A<sup>-1</sup>, along with the Commission Internationale de l'Éclairage (CIE) coordinates of (0.38, 0.59). More recently, Yam and co-workers pioneered the

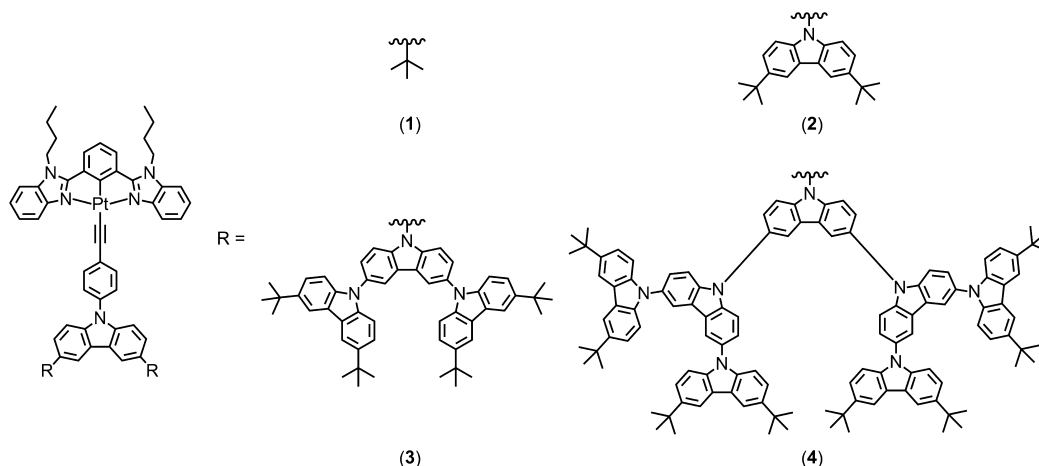
work on cyclometalated alkynylgold(III) dendrimers with carbazole or triphenylamine dendrons.<sup>8</sup> Highly efficient solution-processable PHOLEDs with a saturated yellow emission and a maximum EQE of 10.1% were realized.<sup>8c</sup> The introduction of bipolar moieties to the core unit of the gold(III) dendrimers further improved the device efficiency.<sup>8c</sup> More importantly, the efficiency roll-off value was reduced to less than 1% at the practical brightness level of 1000 cd m<sup>-2</sup>.<sup>8c</sup>

Apart from iridium(III) and gold(III) complexes, cyclometalated platinum(II) complexes are another class of promising phosphorescent emitters because of their high luminescence quantum yields, short excited-state lifetimes, and high thermal and electrochemical stabilities.<sup>2a,3a,6d-g,9-12</sup> Specifically, tridentate cyclometalated platinum(II) complexes represent one of the important candidates for PHOLED application because of their versatility in molecular design and ease of synthesis.<sup>11,12</sup> Vacuum-deposited red-, green-, blue-, and white-emitting PHOLEDs based on platinum(II) complexes have been reported with maximum EQEs of 22.1,<sup>11f</sup> 22.8,<sup>11f</sup> 16.0,<sup>11d</sup> and 11.5%,<sup>11c</sup> respectively. Recently, Che and co-workers reported highly efficient green-emitting solution-processable PHOLEDs based on platinum(II) containing tetradentate dianionic O<sup>-</sup>N<sup>-</sup>C<sup>-</sup>N<sup>-</sup> ligands with promising EQEs.<sup>10b-d</sup> Meanwhile, researchers have attempted to develop platinum(II) dendrimers for solution-processable PHOLEDs. In 2006, Wang and co-workers reported a series of platinum-porphyrin-based dendrimers, and such red-emitting devices exhibited a maximum brightness of up to 600 cd m<sup>-2</sup>.<sup>6d</sup> In

Received: March 11, 2016

Published: May 4, 2016

Scheme 1. Chemical Structures of Alkynylplatinum(II) Complexes 1–4



2015, Li et al. demonstrated another class of platinum(II) dendrimers with bidentate ligands,<sup>6g</sup> and an attractive performance was realized. However, the library of solution-processable platinum(II) complexes is rather small,<sup>6d–g,9f,10c,11g,h,12b,d</sup> and their EL performances are generally inferior to those of vacuum-deposited counterparts. Particularly, platinum(II) dendrimers with cyclometalated tridentate ligands have been less explored in the literature, even though these ligands have been widely studied in the synthesis of small-molecule phosphorescent dopants.<sup>11,12</sup> Herein, we report the design and synthesis of a new class of solution-processable platinum(II) dendrimers with cyclometalated 2,6-bis(*N*-alkylbenzimidazol-2'-yl)benzene *N*<sup>^</sup>*C*<sup>^</sup>*N* tridentate ligand (bzimb) of up to fourth generation. Remarkably, these platinum(II) complexes exhibit high photoluminescence quantum yields (PLQYs) of up to 80% in *N,N'*-dicarbazolyl-3,5-benzene (MCP) thin films. Solution-processable green-emitting PHOLEDs demonstrate a high EQE and current efficiency of up to 10.4% and 37.6 cd A<sup>-1</sup>, respectively, which are comparable to those of the vacuum-deposited devices based on the structurally related platinum(II) bzimb complexes.<sup>12a,b</sup> In addition, the emission energies and CIE coordinates are independent of a wide range of dopant concentrations from 5 to 50%. These platinum(II) complexes can enrich the library of high-efficiency solution-processable metal-containing dendrimers, and the present work demonstrates the first report on the design and synthesis of solution-processable cyclometalated platinum(II) dendrimers with tridentate ligands. In addition, this represents one of the best performances for the solution-processable PHOLEDs based on this class of complexes.<sup>11g,h,12d</sup>

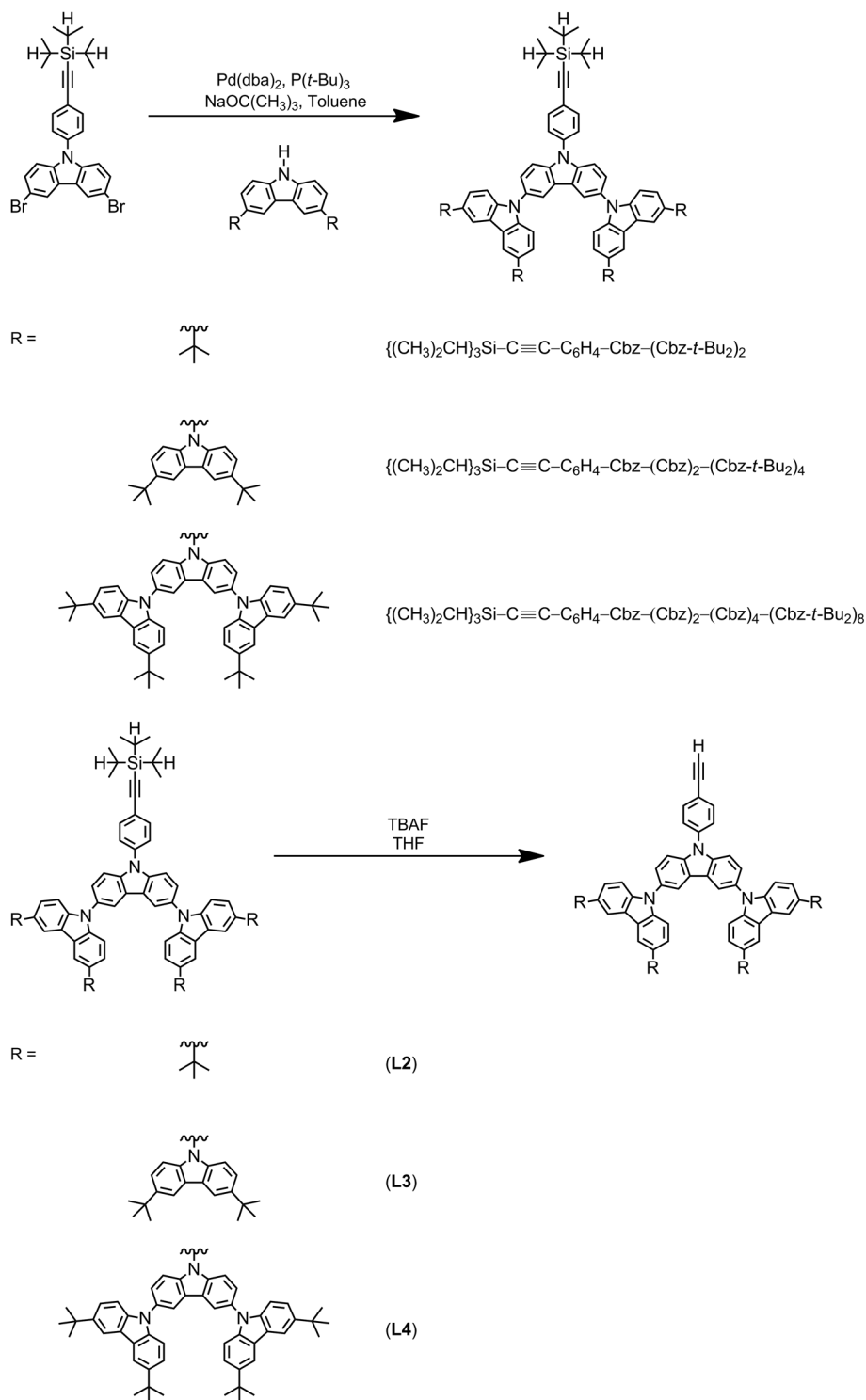
## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The design strategy of platinum(II) dendrimers is built on the incorporation of carbazole dendrons into our previously reported bzimb alkynylplatinum(II) complexes, i.e., [Pt(bzimb)(C≡C–R)], and *tert*-butyl moieties are added as surface groups to increase the solubility. The chemical structures of the dendritic carbazole-containing alkynylplatinum(II) complexes 1–4 are shown in Scheme 1, whereas the synthesis routes for the alkynyl ligands L2–L4 and the alkynylplatinum(II) complexes 1–4 are shown in Schemes 2 and 3, respectively.  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu}_2)_2$ ,  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz}-t\text{-Bu}_2)_4$ ,

and  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz})_4-(\text{Cbz}-t\text{-Bu}_2)_8$  were synthesized by Ullmann reaction between  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CbzBr}_2$ -3,6 and the corresponding carbazole dendrimers,<sup>13</sup> where Cbz, Cbz-*t*-Bu<sub>2</sub>, and  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CbzBr}_2$ -3,6 represent carbazole, 3,6-di-*tert*-butylcarbazole, and 3,6-dibromo-9-[4-((triisopropylsilyl)ethynyl)phenyl]carbazole, respectively. Ligands L2–L4 were synthesized by the deprotection of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu}_2)_2$ ,  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz}-t\text{-Bu}_2)_4$ , and  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz})_4-(\text{Cbz}-t\text{-Bu}_2)_8$  in tetra-*n*-butylammonium fluoride in tetrahydrofuran, respectively.<sup>14</sup> *N*-(4-Ethynylphenyl)-3,6-di-*tert*-butylcarbazole,<sup>15</sup> 2,6-bis(*N*-*n*-butylbenzimidazol-2'-yl)benzene (*n*-Bu<sub>2</sub>bzimb),<sup>12a</sup> and the chloroplatinum(II) precursor, [Pt(*n*-Bu<sub>2</sub>bzimb)Cl],<sup>12a</sup> were prepared by slight modifications of the literature procedures. Complexes 1–4 were synthesized by refluxing the corresponding alkynyl ligands with [Pt(*n*-Bu<sub>2</sub>bzimb)Cl] in the presence of sodium hydroxide, similar to the previously reported procedures.<sup>12b</sup> All complexes were fully characterized by <sup>1</sup>H NMR spectroscopy, FAB-mass spectrometry, IR spectroscopy, and elemental analysis. They were all isolated as air- and thermal-stable yellow or greenish-yellow solids with decomposition temperatures (*T*<sub>d</sub>) above 300 °C, where *T*<sub>d</sub> is defined as the temperature at which the material showed a 5% weight loss (Figure 1). The IR spectra of the complexes feature a weak band at 2084–2086 cm<sup>-1</sup>, corresponding to the  $\nu(\text{C}\equiv\text{C})$  stretching frequency.

**Photophysical Properties.** The electronic absorption spectra and emission spectra of 1–4 in dichloromethane solution at 298 K are shown in Figures 2 and 3 respectively. All complexes show intense vibronic-structured absorption bands at 283–330 nm and moderately intense vibronic-structured absorption bands at 345–410 nm. Similar to the previously reported [Pt(bzimb)(C≡C–R)] complexes<sup>12b,d</sup> and dendritic carbazole-based metal complexes,<sup>7d,e,8a</sup> the higher-energy absorptions are assigned to spin-allowed intraligand (IL)  $\pi \rightarrow \pi^*$  transitions of *n*-Bu<sub>2</sub>bzimb and carbazole units, with the molar extinction coefficients increasing with the carbazole dendrimer generation in the complexes. The lower-energy absorptions are attributed to IL  $\pi \rightarrow \pi^*$  transitions of the *n*-Bu<sub>2</sub>bzimb ligand, with substantial mixing of metal-to-ligand charge transfer (MLCT) [ $d\pi(\text{Pt}) \rightarrow \pi^*(n\text{-Bu}_2\text{bzimb})$ ] and ligand-to-ligand charge transfer (LLCT) [ $\pi(\text{C}\equiv\text{C}-\text{R}) \rightarrow$

Scheme 2. Synthesis Routes of Alkynyl Ligands L2–L4

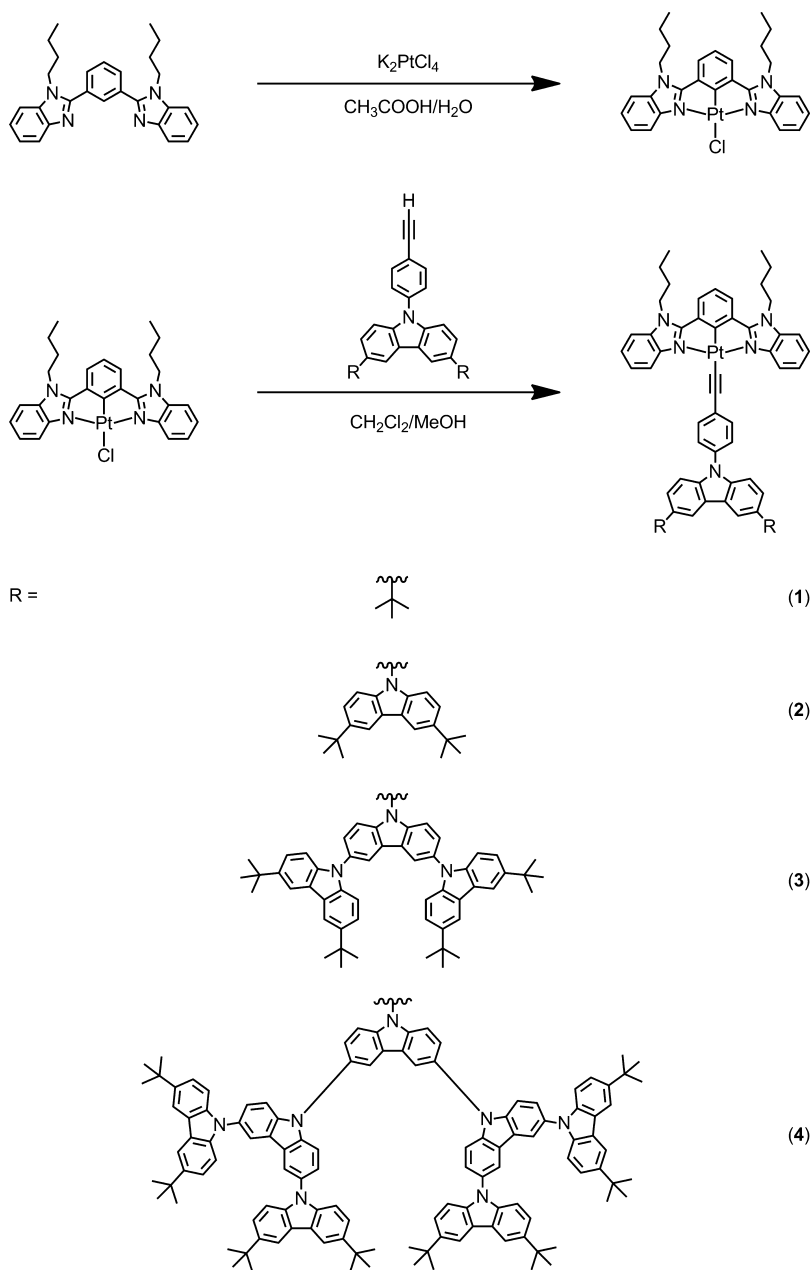


$\pi^*(n\text{-Bu}_2\text{bzimb})$ ] character.<sup>12b,d</sup> The emission spectra of 1–4 in degassed dichloromethane at 298 K are obtained with excitation at  $\lambda \geq 350$  nm. They all show a vibronic-structured emission band with emission maxima at around 512 nm and progressional spacings of about  $1300\text{ cm}^{-1}$ , corresponding to typical aromatic vibrational modes of the *n*-Bu<sub>2</sub>bzimb ligand. The large Stokes shifts and emission lifetimes in the microsecond regime are indicative of emissions of triplet parentage. With reference to our previous studies,<sup>12b,d</sup> the

emission probably originates from the <sup>3</sup>IL [ $\pi \rightarrow \pi^*(n\text{-Bu}_2\text{bzimb})$ ]/MLCT [ $d\pi(\text{Pt}) \rightarrow \pi^*(n\text{-Bu}_2\text{bzimb})$ ] excited state, which is also supported by the insensitivity toward the carbazole dendrimer generation of the alkynyl ligands.

The emission properties for all complexes in poly(methyl methacrylate) (PMMA) thin film at dopant concentrations ranging from 5–50 wt % have also been studied. All complexes show emission profiles similar to their corresponding emission spectra in dichloromethane solution. However, it is noteworthy

Scheme 3. Synthesis Routes of Alkynylplatinum(II) Complexes 1–4



that at 50 wt % dopant concentration, there is an occurrence of a low-energy emission shoulder at around 620 nm as shown in Figure 4. This band is tentatively assigned to the excimeric emission arising from the  $\pi$ - $\pi$  stacking of the *n*-Bu<sub>2</sub>bzimb ligand. A similar observation has been commonly reported in other square-planar metal complexes.<sup>9g,10c,11c,d,f,16</sup> Interestingly, the intensity of this excimeric emission drops as the dendrimer generation increases. This suggests that the intermolecular interaction could be effectively suppressed by the introduction of the carbazole dendrimer, and the reduction is more significant with increasing dendrimer generation. This opens up a new avenue to improve the emission color purity, in contrast to the commonly observed phenomenon for most square-planar metal complexes where excimeric emission becomes dominant in thin films doped with high concentrations.<sup>9g,10c,11c,d,f</sup> Table 1 summarizes the photophysical properties of 1–4. Remarkably, all of the complexes show

high PLQYs of up to 80% in MCP doped thin films, suggesting that they are promising candidates for application in PHOLEDs.

**Electrochemistry.** The cyclic voltammetry of 1–4 in dichloromethane (0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NPF<sub>6</sub>) has been investigated. The electrochemical data of 1–4 are summarized in Table 2, and the representative cyclic voltammograms of 2 are shown in Figure 5. The electrochemical data of the alkyne ligands, including *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole and L2–L4, are summarized in Table 3. In general, an irreversible reduction wave at around -2.00 V versus saturated calomel electrode (SCE) is found for 1–4. The reduction process is assigned as the *n*-Bu<sub>2</sub>bzimb-centered reduction as supported by previous studies as well as the insensitivity toward dendrimer generation.<sup>12b-d</sup> Upon the anodic sweep of 1–4, an irreversible first oxidation wave ranging from +0.74 to +0.92 V vs SCE is observed. This oxidation process is assigned as the

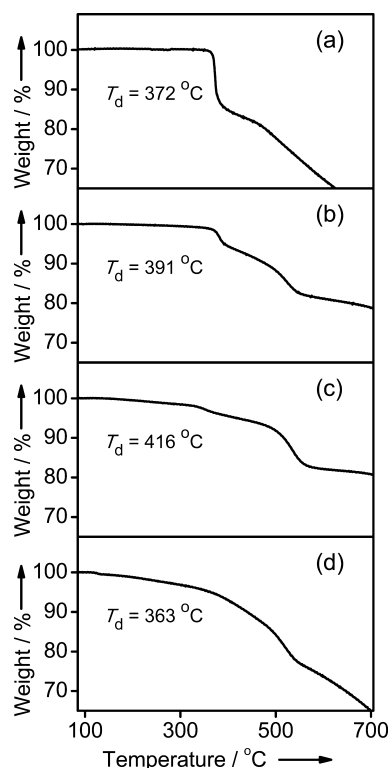


Figure 1. Thermogravimetric curves of (a) 1, (b) 2, (c) 3, and (d) 4.

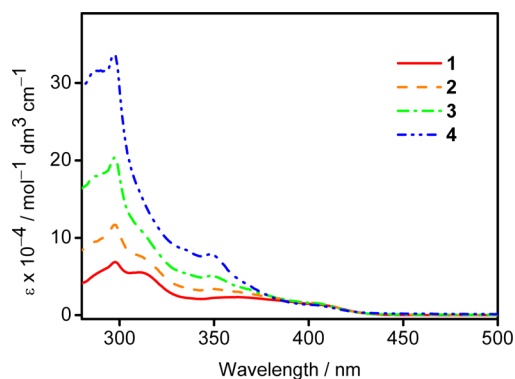


Figure 2. Electronic absorption spectra of 1–4 in  $\text{CH}_2\text{Cl}_2$  at 298 K.

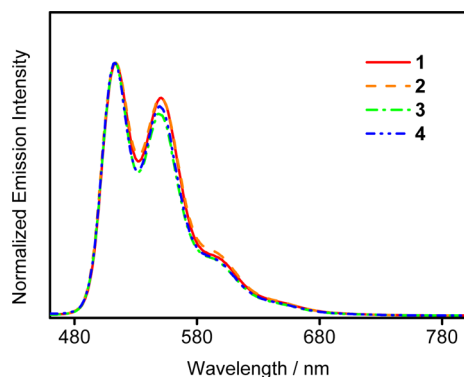


Figure 3. Emission spectra of 1–4 in degassed  $\text{CH}_2\text{Cl}_2$  at 298 K.

alkynyl ligand based oxidation with mixing of a metal-centered contribution, as supported by previous studies.<sup>12b–d</sup> The reduction potential is found to be more positive when the

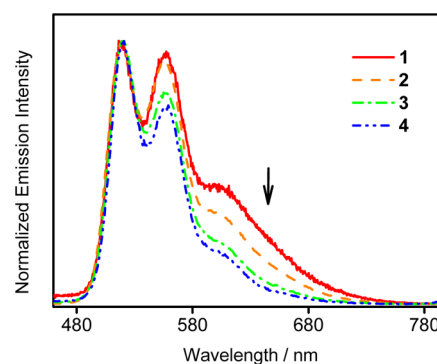


Figure 4. Normalized emission spectra of thin films of 1–4 doped into PMMA at 50 wt % at 298 K.

dendrimer generation increases [1 (+0.74 V vs SCE), 2 (+0.83 V vs SCE), 3 (+0.90 V vs SCE), and 4 (+0.92 V vs SCE)]. The lower-lying highest occupied molecular orbital (HOMO) energy in higher generation dendrimers is attributed to the electron-withdrawing nature of the carbazole dendron with negative inductive effect of the electronegative nitrogen atom.<sup>8a,17</sup> One quasi-reversible oxidation couple at +1.22 V vs SCE is observed for 1, whereas two quasi-reversible oxidation couples at +1.00 to +1.04 V vs SCE and +1.16 to +1.19 V vs SCE are found for 2–4. As reported in the literature,<sup>18</sup> these multiple oxidation processes are attributed to the carbazole-based oxidation. The occurrence of extra oxidation waves in higher generation dendrimers can be ascribed to the oxidation of the carbazole units at the periphery of the dendrimers. Similar redox behaviors are also observed in their corresponding alkynyl ligands as shown in Table 3, providing further evidence for the carbazole-based oxidation process. Similar to the cases of other carbazole-based dendritic iridium(III) and gold(III) complexes,<sup>7e,8a</sup> multiple oxidation processes are also noted. This further confirms the participation of the carbazole dendrons in the electrochemical process and charge transporting properties of this class of complexes.<sup>7d</sup>

**EL Properties.** To study the applicability of 1–4 as phosphorescent dopants for the fabrication of solution-processable PHOLEDs, devices with the configuration of indium tin oxide (ITO)/poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS; 70 nm)/*x* % platinum(II) dendrimer:MCP (60 nm)/2,7-bis(diphenylphosphoryl)-9,9'-spirobifluorene(SPPO13; 30 nm)/LiF (0.8 nm)/Al (100 nm) have been prepared, in which PEDOT:PSS and SPPO13 were used as hole- and electron-transporting layers, respectively. The emissive layer was prepared by spin-coating a solution of platinum(II) dendrimer:MCP blend at different concentrations in dichloromethane. Figure 6 depicts the normalized EL spectra of devices at a current density of 10  $\text{mA cm}^{-2}$ . All devices exhibit vibronic-structured emission, and the EL spectra for all the devices are almost identical to their emission spectra in solution without any undesirable emission coming from the adjacent carrier-transporting layers or the host materials. Remarkably, the CIE coordinates of all devices are almost constant over a wide range of dopant concentrations. For instance, the CIE coordinates of devices made with 1 change from (0.35, 0.60) to (0.36, 0.60) upon increasing the dopant concentration from 5 to 50%. Similar effects have been observed for devices with 2–4 and are in excellent agreement with the emission properties in solution. It is not the case for other square-planar metal complexes, including platinum-

Table 1. Photophysical Properties of Complexes 1–4

complex	absorption $\lambda_{\max}$ (nm) ( $\lambda_{\max}$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ))	medium (T (K))	emission $\lambda_{\max}$ (nm) ( $\tau_o$ ( $\mu\text{s}$ ))	$\Phi_{\text{PL}}(\text{soln})^a$	$\Phi_{\text{PL}}(\text{film})^b$	
1	287 (51500), 298 (67800), 313 (54860), 365 (23310), 406 (14460)	CH <sub>2</sub> Cl <sub>2</sub> (298)	512, 550, 600 (2.4)	0.63		
		glass (77) <sup>c</sup>	499, 535, 575, 630 (7.2)			
		thin film (298)				
		5% in MCP	512, 553, 601			0.71
		10% in MCP	513, 554, 602			0.76
		20% in MCP	513, 554, 602			0.80
		50% in MCP	514, 554, 603			0.58
		2% in PMMA	513, 551, 600			
		4% in PMMA	515, 552, 600			
		8% in PMMA	515, 553, 601			
		20% in PMMA	516, 554, 602			
		50% in PMMA	519, 557, 608			
		2	287 (93920), 298 (115650), 313 (74390), 350 (35210), 403 (16030)			CH <sub>2</sub> Cl <sub>2</sub> (298)
glass (77) <sup>c</sup>	499, 535, 575, 630 (7.3)					
thin film (298)						
5% in MCP	511, 551, 600			0.78		
10% in MCP	511, 551, 600			0.71		
20% in MCP	512, 552, 601			0.70		
50% in MCP	513, 553, 602			0.58		
2% in PMMA	513, 550, 599					
4% in PMMA	514, 550, 599					
8% in PMMA	514, 551, 600					
20% in PMMA	516, 553, 603					
50% in PMMA	519, 556, 606					
3	287 (178750), 297 (201630), 314 (102700), 350 (50470), 403 (16030)			CH <sub>2</sub> Cl <sub>2</sub> (298)	512, 550, 600 (2.6)	0.42
		glass (77) <sup>c</sup>	499, 535, 572, 626 (7.4)			
		thin film (298)				
		5% in MCP	511, 551, 600	0.71		
		10% in MCP	511, 551, 600	0.74		
		20% in MCP	512, 552, 600	0.70		
		50% in MCP	512, 552, 600	0.46		
		2% in PMMA	514, 550, 598			
		4% in PMMA	514, 551, 600			
		8% in PMMA	514, 552, 602			
		20% in PMMA	518, 554, 606			
		50% in PMMA	519, 557, 606			
		4	287 (315690), 297 (336380), 314 (138530), 349 (78780), 402 (13250)	CH <sub>2</sub> Cl <sub>2</sub> (298)	512, 550, 600 (2.7)	
glass (77) <sup>c</sup>	499, 535, 575, 626 (7.2)					
thin film (298)						
5% in MCP	510, 550, 599			0.54		
10% in MCP	510, 550, 599			0.67		
20% in MCP	511, 551, 600			0.64		
50% in MCP	512, 552, 600			0.55		
2% in PMMA	514, 550, 600					
4% in PMMA	515, 551, 600					
8% in PMMA	515, 552, 603					
20% in PMMA	519, 555, 604					
50% in PMMA	520, 557, 605					

<sup>a</sup>Luminescence quantum yield, measured at room temperature using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in degassed aqueous solution as the reference (excitation wavelength = 436 nm,  $\Phi_{\text{lum}} = 0.042$ ). <sup>b</sup>Absolute  $\Phi_{\text{PL}}(\text{film})$  of 1–4 doped into MCP measured using 300 nm as the excitation wavelength. <sup>c</sup>Measured in butyronitrile glass.

(II)<sup>9g,10c,11c,d,f</sup> and gold(III)<sup>16c,d</sup> systems, in which the EL spectra are found to show significant spectral shifts upon dopant aggregation to give a broad red-shifted excimer emission.

More importantly, all the devices demonstrate a promising performance. As depicted in Figure 7, the optimized device made with 1 (i.e., 10%) gave a maximum current efficiency of 29.1 cd A<sup>-1</sup> and a maximum EQE of 8.2%. The incorporation

of carbazole dendron can significantly improve the device performance. In particular, a maximum current efficiency of 37.6 cd A<sup>-1</sup> and a maximum EQE of 10.4% can be achieved for devices with 2. The performance improvement is ascribed to the incorporation of carbazole dendron to improve the hole-transporting property of complex 2, resulting in a better balance in the hole and electron currents at the emissive interface and thus improved device efficiency. As expected, further

Table 2. Electrochemical Data for 1–4<sup>a</sup>

complex	oxidation $E_{1/2}$ (V vs SCE), $\Delta E_p$ (mV), <sup>b</sup> and $[E_{pa}$ (V vs SCE)] <sup>c</sup>	reduction $[E_{pc}$ (V vs SCE)] <sup>d</sup>	$E_{HOMO}$ (eV) <sup>e</sup>	$E_{LUMO}$ (eV) <sup>e</sup>
1	[+0.74], +1.22 (82)	[-1.99]	-5.54	-2.81
2	[+0.83], +1.04 (69), +1.19 (66)	[-2.00]	-5.63	-2.80
3	[+0.90], +1.02 (68), +1.17 (61)	[-1.99]	-5.70	-2.81
4	[+0.92], +1.00 (69), +1.16 (74)	[-2.00]	-5.72	-2.80

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> solution with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> (TBAH) as supporting electrolyte at 298 K; working electrode, glassy carbon. Scan rate = 100 mV s<sup>-1</sup>.  
<sup>b</sup> $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $E_{pa}$  and  $E_{pc}$  are the peak anodic and peak cathodic potentials, respectively.  $\Delta E_p = (E_{pa} - E_{pc})$ .  
<sup>c</sup> $E_{pa}$  refers to the anodic peak potential for the irreversible oxidation waves. <sup>d</sup> $E_{pc}$  refers to the cathodic peak potential for the irreversible reduction waves. <sup>e</sup> $E_{HOMO}$  and  $E_{LUMO}$  levels were calculated from electrochemical potentials, i.e.,  $E_{HOMO} = -e(4.8 \text{ V} + E_{pa})$  and  $E_{LUMO} = -e(4.8 \text{ V} + E_{pc})$ .

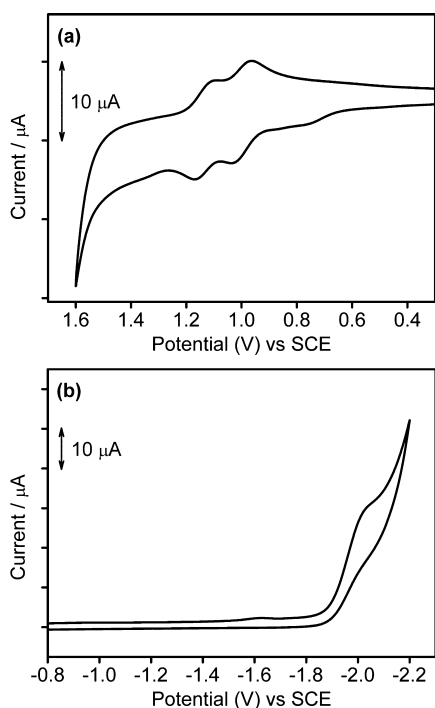


Figure 5. Cyclic voltammograms for the (a) oxidation and (b) reduction scans of 2 in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>).

Table 3. Electrochemical Data for Alkynyl Ligands, *N*-(4-Ethynylphenyl)-3,6-di-*tert*-butylcarbazole, and L2–L4<sup>a</sup>

ligand	$E_{1/2}$ (V vs SCE) ( $\Delta E_p$ (mV)) <sup>b</sup>
<i>N</i> -(4-ethynylphenyl)-3,6-di- <i>tert</i> -butylcarbazole	+1.21 (90)
L2	+1.00 (62), +1.14 (52)
L3	+0.99 (63), +1.14 (65)
L4	+0.98 (63), +1.13 (69)

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> solution with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> (TBAH) as supporting electrolyte at 298 K; working electrode, glassy carbon. Scan rate = 100 mV s<sup>-1</sup>. <sup>b</sup> $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $E_{pa}$  and  $E_{pc}$  are the peak anodic and peak cathodic potentials, respectively.  $\Delta E_p = (E_{pa} - E_{pc})$ .

introduction of carbazole dendrons to the phosphorescent core to form higher generation dendrimers has been found to lower the device performance, i.e., maximum EQE = 6.0 and 4.7% for devices with 3 and 4, respectively. In contrast, the charge transport ability is improved with increasing dendrimer generation, as reflected by the lower driving voltage of 10% doped devices (Figure 8). However, this improved charge transporting properties would inevitably lead to a lowering of the device performance, along with the lower PLQYs in thin films doped with 3 and 4. Table 4 summarizes the key

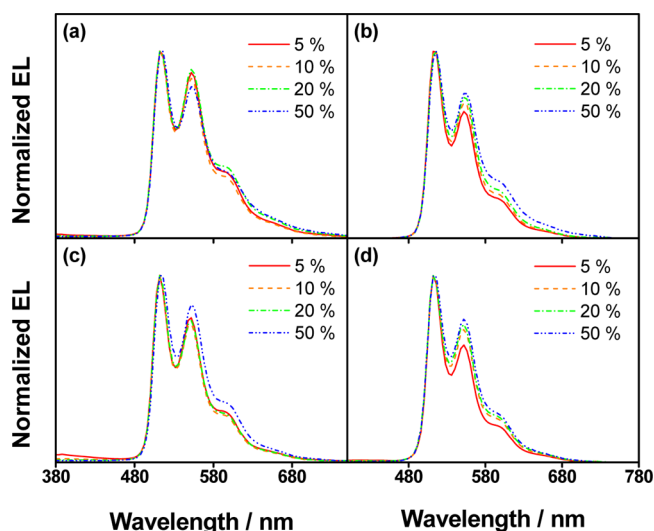


Figure 6. EL spectra of devices made with (a) 1, (b) 2, (c) 3, and (d) 4 at a current density of 10 mA cm<sup>-2</sup>.

parameters of devices made with 1–4. It should be highlighted that the EQEs of the present devices based on platinum(II) dendrimers are comparable to those of the vacuum-deposited devices based on the structurally related platinum(II) bzimb complexes<sup>14a,b</sup> and are one of the highest values for PHOLEDs based on metal-containing dendrimers (Table 5). In addition, the present results represent the first report on the design and synthesis of platinum(II) dendrimers with tridentate ligands.

## CONCLUSIONS

A new class of dendritic carbazole-containing alkynylplatinum(II) complexes of up to fourth generation has been successfully designed and synthesized. The incorporation of carbazole dendrimers can significantly suppress intermolecular interactions of the complexes while retaining their high PLQYs of up to 80% in solid-state thin films. More importantly, high-performance solution-processable PHOLEDs with a remarkable maximum current efficiency and EQE of 37.6 cd A<sup>-1</sup> and 10.4%, respectively, have been realized, which are the highest ever reported values for solution-processable PHOLEDs based on platinum(II) complexes with tridentate ligands, and this work represents the first demonstration of the application studies of platinum(II) dendrimers with tridentate ligands in PHOLEDs.

## EXPERIMENTAL SECTION

**Material and Reagents.** 3,6-Dibromo-9-(4-((triisopropylsilyl)ethynyl)phenyl)carbazole,<sup>19</sup> 3,6-di(*tert*-butyl-carbazolyl)carbazole,<sup>20</sup> and 3,6-bis-[3,6-di(*tert*-butylcarbazolyl)]carbazole<sup>7e</sup> were synthesized according to reported procedures with slight modifications. All

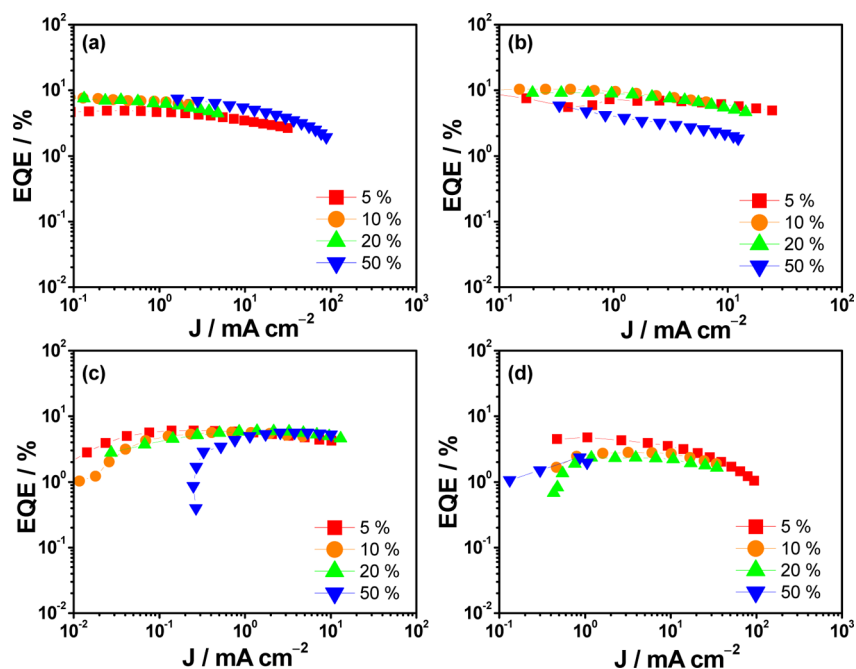


Figure 7. EQEs of devices made with 1–4 at different dopant concentrations.

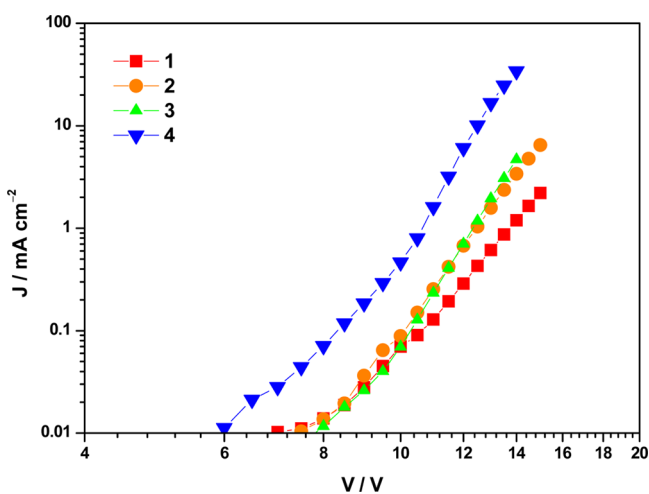


Figure 8. Current density–voltage characteristics of 10% doped devices with 1–4.

solvents were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as received. Tetra-*n*-butylammonium hexafluorophosphate (Aldrich, 98%) was recrystallized no less than three times from hot absolute ethanol prior to use.

**Synthesis of Precursor Ligands and Alkynyl Ligands.** All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$ . To a well-degassed solution of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CbzBr}_{2-3,6}$  (1.02 g, 1.75 mmol), 3,6-di-*tert*-butylcarbazole (1.03 g, 3.69 mmol), sodium *tert*-butoxide (510 mg, 5.27 mmol), and tris(dibenzylideneacetone)dipalladium(0) (161 mg, 0.18 mmol) in toluene (10 mL) was added tri-*tert*-butylphosphine (35 mg, 0.18 mmol). The resulting mixture was stirred and heated to reflux at 120 °C for 24 h. To the mixture was then added deionized water (20 mL). The organic phase was separated, washed with brine solution for three times, and then extracted three times with dichloromethane. The organic extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. Further purification was done by column chromatography (70–230 mesh) using hexane–

Table 4. Key Parameters of Devices Made with 1–4

complex	dopant concentration (wt %)	max. current efficiency ( $\text{cd A}^{-1}$ )	max. power efficiency ( $\text{lm W}^{-1}$ )	max. EQE (%)	CIE ( $x, y$ ) <sup>a</sup>
1	5	17.2	4.8	4.9	0.35, 0.60
	10	29.1	9.1	8.2	0.35, 0.61
	20	26.7	8.0	7.7	0.36, 0.60
	50	25.2	11.3	7.5	0.36, 0.60
2	5	32.8	11.4	9.1	0.32, 0.63
	10	37.6	11.4	10.4	0.33, 0.62
	20	33.1	11.5	9.2	0.33, 0.62
	50	20.5	8.1	5.9	0.35, 0.61
3	5	21.4	7.1	6.0	0.33, 0.61
	10	20.4	5.5	5.8	0.32, 0.62
	20	21.4	6.3	6.0	0.33, 0.62
	50	20.2	5.7	5.7	0.35, 0.61
4	5	16.7	6.2	4.7	0.31, 0.62
	10	10.0	2.8	2.8	0.32, 0.62
	20	8.3	2.3	2.4	0.32, 0.61
	50	8.4	2.0	2.4	0.33, 0.61

<sup>a</sup>CIE coordinates are taken at a current density of 10  $\text{mA cm}^{-2}$ .

dichloromethane (6:1, v/v) as eluent. Subsequent recrystallization by diffusion of diethyl ether vapor into a concentrated solution of the product gave  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$  as a white solid. Yield: 600 mg, 35%. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ , 298 K, relative to  $\text{Me}_4\text{Si}$ ,  $\delta$ ) 1.19 (s, 21H,  $-\text{Si}\{(\text{CH}(\text{CH}_3)_2)_3\}$ ), 1.46 (s, 36H, *tert*-butyl protons), 7.33 (d,  $J = 8.6$  Hz, 4H, carbazolyl protons), 7.45 (dd,  $J = 8.6$  and 2.0 Hz, 4H, carbazolyl protons), 7.58–7.65 (m, 4H, carbazolyl protons), 7.69 (d,  $J = 8.6$  Hz, 2H, phenyl protons), 7.81 (d,  $J = 8.6$  Hz, 2H, phenyl protons), 8.16 (d,  $J = 2.0$  Hz, 4H, carbazolyl protons), 8.23 (d,  $J = 1.7$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  978  $[\text{M}]^+$ . Elemental analysis: Found (%): C, 84.08; H, 8.15; N, 4.19. Calcd for  $\text{C}_{69}\text{H}_{79}\text{N}_3\text{Si}\cdot 0.5\text{H}_2\text{O}$ : C, 83.92; H, 8.17; N, 4.26.

$\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz}-t\text{-Bu})_4$ . This was synthesized according to a procedure similar to that of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$  except that 3,6-di(*tert*-butylcarbazolyl)carbazole (1.21 g, 1.67 mmol) was used in place



**Table 5. Key Parameters of Solution-Processable PHOLEDs Based on Metal-Containing Dendrimers**

metal core	max. current efficiency (cd A <sup>-1</sup> )	max. power efficiency (lm W <sup>-1</sup> )	max. EQE (%)	$\lambda_{\text{max}}$ (nm)	CIE (x, y)	ref
Re(I)	0.8	0.2	0.4	601		6a
Au(III)	3.3	3.5	3.6	636	0.46, 0.36	8b
Pt(II)	22.1	12.3	11.7	608	0.56, 0.42	6g
Pt(II)	17.5	8.4		544	0.39, 0.56	6e
Pt(II)	29.3	21.7	9.0	504	0.33, 0.58	6f
Au(III)	31.1	22.6	10.1	546	0.40, 0.55	8c
Ir(III)	57.9		16.6	528	0.38, 0.59	7e
Pt(II)	37.6	11.4	10.4	510	0.33, 0.62	this work

of 3,6-di-*tert*-butylcarbazole. A white solid of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz}-t\text{-Bu})_4$  was obtained. Yield: 400 mg, 27%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.22 (s, 21H,  $-\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$ ), 1.47 (s, 72H, *tert*-butyl protons), 7.35 (d,  $J = 8.8$  Hz, 8H, carbazolyl protons), 7.46 (dd,  $J = 8.8$  and 1.4 Hz, 8H, carbazolyl protons), 7.60–7.66 (m, 8H, carbazolyl protons), 7.76–7.90 (m, 8H, carbazolyl and phenyl protons), 8.17 (d,  $J = 1.4$  Hz, 8H, carbazolyl protons), 8.28 (d,  $J = 1.5$  Hz, 4H, carbazolyl protons), 8.55 (d,  $J = 1.7$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  1861 [M]<sup>+</sup>. Elemental analysis: Found (%): C, 84.86; H, 7.63; N, 5.13. Calcd for C<sub>133</sub>H<sub>139</sub>N<sub>7</sub>Si<sub>2</sub>H<sub>2</sub>O: C, 84.89; H, 7.55; N, 5.21.

$\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz})_4-(\text{Cbz}-t\text{-Bu})_8$ . This was synthesized according to a procedure similar to that of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$  except that 3,6-bis-[3,6-di(*tert*-butylcarbazolyl)]carbazole (2.1 g, 1.31 mmol) was used in place of 3,6-di-*tert*-butylcarbazole. A white solid of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz})_4-(\text{Cbz}-t\text{-Bu})_8$  was obtained. Yield: 500 mg, 21%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.25 (s, 21H,  $-\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$ ), 1.53 (s, 144H, *tert*-butyl protons), 7.35 (d,  $J = 8.8$  Hz, 16H, carbazolyl protons), 7.45 (dd,  $J = 8.8$  and 1.2 Hz, 16H, carbazolyl protons), 7.61 (dd,  $J = 8.8$  and 1.7 Hz, 8H, carbazolyl protons), 7.68 (d,  $J = 8.8$  Hz, 8H, carbazolyl protons), 7.83–7.97 (m, 16H, phenyl and carbazolyl protons), 8.17 (d,  $J = 1.2$  Hz, 16H, carbazolyl protons), 8.28 (d,  $J = 1.7$  Hz, 8H, carbazolyl protons), 8.61 (d,  $J = 1.5$  Hz, 4H, carbazolyl protons), 8.71 (d,  $J = 1.5$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  3634 [M]<sup>+</sup>. Elemental analysis: Found (%): C, 82.16; H, 7.23; N, 5.41. Calcd for C<sub>261</sub>H<sub>259</sub>N<sub>15</sub>Si<sub>2</sub>SCH<sub>2</sub>Cl<sub>2</sub>: C, 82.28; H, 6.92; N, 5.46.

**Ligand L2.** To a solution of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$  (300 mg, 0.31 mmol) and tetrahydrofuran (30 mL) was added a solution of tetra-*n*-butylammonium fluoride (0.1 M) in THF (3.1 mL). The solution was stirred for 4 h under nitrogen, and the solvent was removed. The residue was purified by column chromatography on silica gel (70–230 mesh) using hexane–dichloromethane (6:1, v/v) as the eluent to give L2 as a white solid. Yield: 210 mg, 83%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.46 (s, 36H, *tert*-butyl protons), 3.23 (s, 1H, HC≡CC<sub>6</sub>H<sub>4</sub>), 7.33 (d,  $J = 8.8$  Hz, 4H, carbazolyl protons), 7.45 (dd,  $J = 8.8$  and 1.5 Hz, 4H, carbazolyl protons), 7.59–7.67 (m, 4H, carbazolyl protons), 7.72 (d,  $J = 8.3$  Hz, 2H, phenyl protons), 7.83 (d,  $J = 8.3$  Hz, 2H, phenyl protons), 8.16 (d,  $J = 1.5$  Hz, 4H, carbazolyl protons), 8.23 (d,  $J = 1.2$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  822 [M]<sup>+</sup>. Elemental analysis: Found (%): C, 86.69; H, 7.59; N, 4.98. Calcd for C<sub>60</sub>H<sub>59</sub>N<sub>3</sub>·0.5H<sub>2</sub>O: C, 86.71; H, 7.28; N, 5.06.

**Ligand L3.** This was synthesized according to a procedure similar to that of L2 except that  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz}-t\text{-Bu})_4$  (300 mg, 0.16 mmol) was used in place of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$ . A white solid of L3 was obtained. Yield: 220 mg, 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.45 (s, 72H, *tert*-butyl protons), 3.28 (s, 1H, HC≡CC<sub>6</sub>H<sub>4</sub>), 7.34 (d,  $J = 8.8$  Hz, 8H, carbazolyl protons), 7.45

(dd,  $J = 8.8$  and 2.0 Hz, 8H, carbazolyl protons), 7.60 (dd,  $J = 8.6$  and 1.7 Hz, 4H, carbazolyl protons), 7.64 (d,  $J = 8.6$  Hz, 4H, carbazolyl protons), 7.78–7.90 (m, 8H, carbazolyl and phenyl protons), 8.15 (d,  $J = 2.0$  Hz, 8H, carbazolyl protons), 8.26 (d,  $J = 1.7$  Hz, 4H, carbazolyl protons), 8.54 (d,  $J = 1.7$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  1706 [M]<sup>+</sup>. Elemental analysis: Found (%): C, 86.04; H, 7.23; N, 5.68. Calcd for C<sub>124</sub>H<sub>119</sub>N<sub>7</sub>H<sub>2</sub>O: C, 86.32; H, 7.07; N, 5.68.

**Ligand L4.** This was synthesized according to a procedure similar to that of L2 except that  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz})_2-(\text{Cbz})_4-(\text{Cbz}-t\text{-Bu})_8$  (400 mg, 0.11 mmol) was used in place of  $\{(\text{CH}_3)_2\text{CH}\}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2$ . A white solid of L4 was obtained. Yield: 300 mg, 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.49 (s, 144H, *tert*-butyl protons), 3.34 (s, 1H, HC≡CC<sub>6</sub>H<sub>4</sub>), 7.38 (d,  $J = 8.8$  Hz, 16H, carbazolyl protons), 7.48 (dd,  $J = 8.8$  and 1.2 Hz, 16H, carbazolyl protons), 7.65 (dd,  $J = 8.8$  and 1.7 Hz, 8H, carbazolyl protons), 7.70 (d,  $J = 8.8$  Hz, 8H, carbazolyl protons), 7.85–8.00 (m, 16H, phenyl and carbazolyl protons), 8.19 (d,  $J = 1.2$  Hz, 16H, carbazolyl protons), 8.31 (d,  $J = 1.7$  Hz, 8H, carbazolyl protons), 8.64 (d,  $J = 1.5$  Hz, 4H, carbazolyl protons), 8.74 (d,  $J = 1.5$  Hz, 2H, carbazolyl protons). Positive FAB-MS:  $m/z$  3477 [M]<sup>+</sup>. Elemental analysis: Found (%): C, 85.82; H, 7.36; N, 5.84. Calcd for C<sub>252</sub>H<sub>239</sub>N<sub>15</sub>·3CH<sub>3</sub>OH: C, 85.70; H, 7.08; N, 5.88.

**Synthesis of Alkynylplatinum(II) Complexes.** All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[\text{Pt}(n\text{-Bu}_2\text{bzimb})\{\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-t\text{-Bu}_2\}]$  (1). This was synthesized according to a modified literature procedure for platinum(II) bzimb complexes reported previously by Yam and co-workers.<sup>12b</sup> A mixture of *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole (100 mg, 0.33 mol) and sodium hydroxide (40 mg, 0.99 mol) was allowed to stir in degassed methanol solution (5 mL) for 30 min. Then, a solution of  $[\text{Pt}(n\text{-Bu}_2\text{bzimb})\text{Cl}]$  (215 mg, 0.33 mol) in degassed dichloromethane (20 mL) was added, and the resultant solution was refluxed for 12 h. After filtration, the yellow precipitate was washed with water, methanol, and diethyl ether. Subsequent recrystallization by diffusing diethyl ether into a concentrated dichloromethane solution of the product gave 1 as a yellow solid. Yield: 260 mg, 75%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 0.93 (t,  $J = 7.3$  Hz, 6H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.43 (s, 18H, *tert*-butyl protons), 1.42–1.46 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.90–1.92 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.83 (t,  $J = 7.3$  Hz, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.40 (d,  $J = 8.6$  Hz, 2H, carbazolyl protons), 7.43–7.46 (m, 3H, benzimidazolyl and phenyl protons), 7.49–7.51 (m, 4H, benzimidazolyl and carbazolyl protons), 7.59 (d,  $J = 8.1$  Hz, 2H, phenyl protons), 7.71 (d,  $J = 8.1$  Hz, 2H, phenyl protons), 7.87 (d,  $J = 8.1$  Hz, 2H, phenyl protons), 7.93 (d,  $J = 8.1$  Hz, 2H, benzimidazolyl protons), 8.29 (d,  $J = 1.5$  Hz, 2H, carbazolyl protons), 8.97 (d,  $J = 8.1$  Hz, 2H, benzimidazolyl protons). Positive FAB-MS:  $m/z$  994 [M]<sup>+</sup>. IR (KBr disk): 2084 cm<sup>-1</sup>  $\nu(\text{C}\equiv\text{C})$ . Elemental analysis: Found (%): C, 66.87; H, 5.83; N, 6.99. Calcd for C<sub>36</sub>H<sub>37</sub>N<sub>3</sub>Pt·0.5H<sub>2</sub>O: C, 66.98; H, 5.82; N, 6.97.

$[\text{Pt}(n\text{-Bu}_2\text{bzimb})\{\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{Cbz}-(\text{Cbz}-t\text{-Bu})_2\}]$  (2). This was synthesized according to a procedure similar to that of complex 1 except that L2 (200 mg, 0.24 mmol) was used in place of *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole. A yellow solid of 2 was obtained. Yield: 300 mg, 85%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ ) 1.04 (t,  $J = 7.4$  Hz, 6H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.46 (s, 36H, *tert*-butyl protons), 1.55–1.59 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.03–2.07 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.68 (t,  $J = 7.4$  Hz, 4H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.38 (d,  $J = 8.7$  Hz, 4H, carbazolyl protons), 7.41 (t,  $J = 8.1$  Hz, 1H, phenyl proton), 7.44–7.46 (d,  $J = 7.9$  Hz, 2H, benzimidazolyl protons), 7.48 (dd,  $J = 8.7$  and 1.5 Hz, 4H, carbazolyl protons), 7.51–7.54 (m, 4H, benzimidazolyl protons), 7.66 (dd,  $J = 8.7$  and 2.0 Hz, 2H, carbazolyl protons), 7.73–7.75 (m, 4H, phenyl protons), 7.79 (d,  $J = 8.7$  Hz, 2H, carbazolyl protons), 7.94 (d,  $J = 8.3$  Hz, 2H, phenyl protons), 8.18 (d,  $J = 1.5$  Hz, 4H, carbazolyl protons), 8.29 (d,  $J = 2.0$  Hz, 2H, carbazolyl protons), 9.12 (d,  $J = 7.9$  Hz, 2H, benzimidazolyl protons). Positive FAB-MS:  $m/z$  1437 [M]<sup>+</sup>. IR (KBr disk): 2084 cm<sup>-1</sup>  $\nu(\text{C}\equiv\text{C})$ . Elemental analysis: Found (%): C, 72.33; H, 5.98; N, 6.62. Calcd for C<sub>88</sub>H<sub>87</sub>N<sub>7</sub>Pt·H<sub>2</sub>O: C, 72.60; H, 6.16; N, 6.74.

[Pt(*n*-Bu<sub>2</sub>bzimb)](C≡C-C<sub>6</sub>H<sub>4</sub>-Cbz-Cbz<sub>2</sub>-(Cbz-*t*-Bu)<sub>2</sub>)] (3). This was synthesized according to a procedure similar to that of complex 1 except that L3 (200 mg, 0.12 mmol) was used in place of *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole. A greenish-yellow solid of 3 was obtained. Yield: 205 mg, 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si, δ) 1.05 (t, *J* = 7.4 Hz, 6H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.44 (s, 72H, *tert*-butyl protons), 1.54–1.60 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.04–2.09 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.69 (t, *J* = 7.4 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.32–7.38 (m, 10H, benzimidazolyl and carbazolyl protons), 7.41–7.47 (m, 11H, benzimidazolyl, carbazolyl and phenyl protons), 7.55 (t, *J* = 8.2 Hz, 2H, benzimidazolyl protons), 7.64 (dd, *J* = 8.7 and 1.9 Hz, 4H, carbazolyl protons), 7.73 (d, *J* = 8.7 Hz, 4H, carbazolyl protons), 7.76 (d, *J* = 8.7 Hz, 2H, phenyl protons), 7.81 (d, *J* = 8.4 Hz, 2H, phenyl protons), 7.89 (dd, *J* = 8.7 and 1.9 Hz, 2H, carbazolyl protons), 7.95 (d, *J* = 8.7 Hz, 2H, carbazolyl protons), 8.00 (d, *J* = 8.4 Hz, 2H, phenyl protons), 8.17 (d, *J* = 1.5 Hz, 8H, carbazolyl protons), 8.31 (d, *J* = 1.9 Hz, 4H, carbazolyl protons), 8.59 (d, *J* = 1.9 Hz, 2H, carbazolyl protons), 9.14 (d, *J* = 8.2 Hz, 2H, benzimidazolyl protons). Positive FAB-MS: *m/z* 2323 [M]<sup>+</sup>. IR (KBr disk): 2086 cm<sup>-1</sup> ν(C≡C). Elemental analysis: Found (%): C, 74.93; H, 6.20; N, 6.54. Calcd for C<sub>152</sub>H<sub>147</sub>N<sub>11</sub>Pt·CHCl<sub>3</sub>: C, 75.24; H, 6.11; N, 6.31.

[Pt(*n*-Bu<sub>2</sub>bzimb)](C≡C-C<sub>6</sub>H<sub>4</sub>-Cbz-Cbz<sub>2</sub>-Cbz<sub>4</sub>-(Cbz-*t*-Bu)<sub>8</sub>)] (4). This was synthesized according to a procedure similar to that of complex 1 except that L4 (250 mg, 0.08 mmol) was used in place of *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole. A greenish-yellow solid of 4 was obtained. Yield: 220 mg, 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si, δ) 1.04 (t, *J* = 7.3 Hz, 6H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.28–1.30 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.43 (s, 144H, *tert*-butyl protons), 2.04–2.07 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.66 (t, *J* = 7.3 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.31–7.46 (m, 35H, benzimidazolyl and carbazolyl protons), 7.52–7.69 (m, 20H, benzimidazolyl and carbazolyl protons), 7.79–7.87 (m, 12H, carbazolyl and phenyl protons), 7.92 (dd, *J* = 8.6 and 1.8 Hz, 2H, carbazolyl protons), 8.00 (d, *J* = 8.6 Hz, 2H, carbazolyl protons), 8.06 (d, *J* = 8.3 Hz, 2H, phenyl protons), 8.12 (d, *J* = 1.7 Hz, 16H, carbazolyl protons), 8.25 (d, *J* = 1.6 Hz, 8H, carbazolyl protons), 8.57 (d, *J* = 1.8 Hz, 4H, carbazolyl protons), 8.69 (d, *J* = 1.8 Hz, 2H, carbazolyl protons), 9.21 (d, *J* = 8.3 Hz, 2H, benzimidazolyl protons). Positive FAB-MS: *m/z* 4093 [M]<sup>+</sup>. IR (KBr disk): 2085 cm<sup>-1</sup>. Elemental analyses: Found (%): C, 76.33; H, 6.28; N, 5.99. Calcd for C<sub>280</sub>H<sub>267</sub>N<sub>19</sub>Pt·3CHCl<sub>3</sub>: C, 76.36; H, 6.11; N, 5.98.

**Physical Measurements and Instrumentation.** The UV–vis absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with a Xenon flash lamp. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or Bruker DPX-400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane. Positive FAB mass spectra were recorded on a Thermo Scientific DFS High-Resolution Magnetic Sector Mass Spectrometer. IR spectra were recorded as KBr disk on a Bio-Rad FTS-7 FTIR spectrometer (4000–400 cm<sup>-1</sup>). Elemental analyses were performed on the Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing. Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Liquid nitrogen was placed into the quartz-walled optical Dewar flask for low-temperature (77 K) photophysical measurements. Excited-state lifetimes of solution and glass samples were measured using a conventional laser system. The excitation source used was the 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS s<sup>-1</sup>) digital oscilloscope and analyzed by using a program for exponential fits. Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.<sup>21a</sup> A degassed solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in aqueous state (Φ<sub>lum</sub> = 0.042, excitation wavelength at 436 nm) was used as the reference,<sup>21b</sup> whereas those of the thin films were measured on a Hamamatsu

C9920–03 Absolute PL Quantum Yield Measurement System. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc., model CHI 600A electrochemical analyzer. All solutions for electrochemical studies were deaerated with prepurified argon gas just before measurements. Thermal analyses were performed with the PerkinElmer TAC7/DX thermal analysis controller, in which *T<sub>d</sub>* is defined as the temperature at which the material showed a 5% weight loss. For PHOLED fabrication, devices with the structure of ITO/PEDOT:PSS (70 nm)/emissive layer (60 nm)/SPPO13 (30 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated, in which the emissive layer was formed by mixing the dendrimer with MCP to prepare a 10 mg cm<sup>-3</sup> solution in chloroform via a spin-coating technique. Current density–voltage–luminance characteristics of devices were simultaneously measured by a programmable Keithley 2420 source meter and a PR-655 colorimeter. All devices were measured under ambient conditions without encapsulation.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

V.W.-W.Y. acknowledges support from The University of Hong Kong and the URC Strategic Research Theme on New Materials. The work described in this paper was fully supported by a grant from the Theme-Based Research Scheme of the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. T23-713/11). F.K.-W.K. and Y.-C.W. acknowledge the receipt of postgraduate studentships from The University of Hong Kong. F.K.-W.K. acknowledges the receipt of a University Postgraduate Fellowship from The University of Hong Kong.

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