Dendrimers

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Dendritic Luminescent Gold(III) Complexes for Highly Efficient Solution-Processable Organic Light-Emitting Devices**

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Organic light-emitting diodes (OLEDs) have attracted much attention in the past few decades and are considered as remarkably attractive candidates for flat panel display technologies and solid-state lighting.[1] Phosphorescent heavy-metal complexes, such as iridium(III), platinum(II), ruthenium(II), and osmium(II) complexes, are important classes of materials for making OLEDs because of their high luminescence quantum yields.[2] The presence of a heavy-metal center can effectively enhance spin-orbit coupling and promotes an efficient intersystem crossing from its singlet excited state to the triplet excited state, harvesting both singlet and triplet excitons for light emission to realize an internal quantum efficiency of up to 100%.[3] The performance of multilayer OLEDs based on vacuum-deposited phosphorescent small molecules of iridium(III) complexes are very encouraging.[2a,b] However, the architecture of such devices is rather complicated and requires a delicate control of the dopant concentration, thereby leading to a high production cost. The use of solution processing techniques including spin-coating or ink-jet printing to prepare OLEDs is an effective approach to lower the manufacturing cost, especially for large-area displays.[4] Indeed, various classes of small molecules and conjugated polymers have been reported to give highly efficient solution-processable OLEDs.[1b,5]

Recent demonstrations of the design and synthesis of phosphorescent dendrimers have opened up a new and interesting direction for the preparation of solution-processable phosphorescent OLEDs (PHOLEDs).[6] The corresponding carbazole-based phosphorescent dendrimers have been successfully synthesized by incorporating the iridium(III) emitter within a dendritic structure.[7] In such dendrimers, the *tert*-butyl surface groups and carbazole dendrons can effectively enhance the solubility as well as minimize the intermolecular interactions between the molecules that lead to emission quenching or triplet–triplet annihilation.[8] Solution-processable PHOLEDs based on these iridium(III) dendrimers have been prepared with a high external quantum efficiency (EQE) of 16.6%.[7a] Apart from the iridium(III),[6c–e] ruthenium(II),[6f] and rhenium(I)[6g] systems, there have been no reports on the synthesis of dendrimers with other heavy-metal centers for the fabrication of PHOLEDs; for example, platinum(II) and gold(III) metal centers, which are anticipated to give interesting photophysical properties.

Our research group has developed new classes of phosphorescent cyclometalated alkynylgold(III) complexes,[9,10] some of which are thermally stable and have been utilized as dopants for the fabrication of highly efficient PHOLEDs.[9b,d] The optimized device was found to exhibit a high EQE of 11.5% and a current efficiency of 37.4 cd A^{-1}.[9d] Since gold complexes are relatively nontoxic and environmentally benign, such alkynylgold(III) complexes are envisaged to be promising candidates for the exploration of new classes of transition-metal-containing dendrimers for the development of high-efficiency solution-processable OLEDs. Herein, we report the design, synthesis, as well as photophysical and electroluminescence properties of a new class of solution-processable phosphorescent carbazole-based dendritic alkynylgold(III) complexes **1**–**3** and their applications in the fabrication of PHOLEDs. Complexes **1**–**3** (Scheme 1) were characterized by ^{1}H NMR spectroscopy, FAB mass spectrometry, IR spectroscopy, and elemental analyses. These new dendrimers have been isolated as thermally stable solids with deposition temperatures above 400 °C.

The UV/Vis absorption spectra of **1**–**3** in dichloromethane at 298 K show intense vibronic-structured absorption bands at 242–350 nm, with a shoulder at about 390–410 nm and an absorption tail at 430–500 nm (see Figure S1 in the Supporting Information). The absorption bands at 242–350 nm are mainly attributed to spin-allowed intraligand (IL) $\pi\rightarrow\pi^*$ transitions of the carbazole units.[7,11] Similar to our previously reported alkynylgold(III) compounds, the weaker vibronic-structured absorption band is tentatively assigned to a metal-perturbed IL $\pi\rightarrow\pi^*$ transition of the cyclometalated (2,5-F_2–C_6H_3–C^N^C) ligand with charge-transfer character from the phenyl ring to the pyridyl unit. However, since the complexes have 3,6-di-*tert*-butylcarbazole substituents at the 4,4′-positions of the triphenylamine alkynyl moieties, an admixture of IL $\pi\rightarrow\pi^*$ transitions of the 2,5-F_2–C_6H_3–C^N^C and alkynyltriarylamine ligands as well as a ligand-to-ligand charge transfer (LLCT) π[alkynyltriarylamine]$\rightarrow\pi^*$[2,5-F_2–C_6H_3–C^N^C] transition are likely to occur at similar energies.[9]

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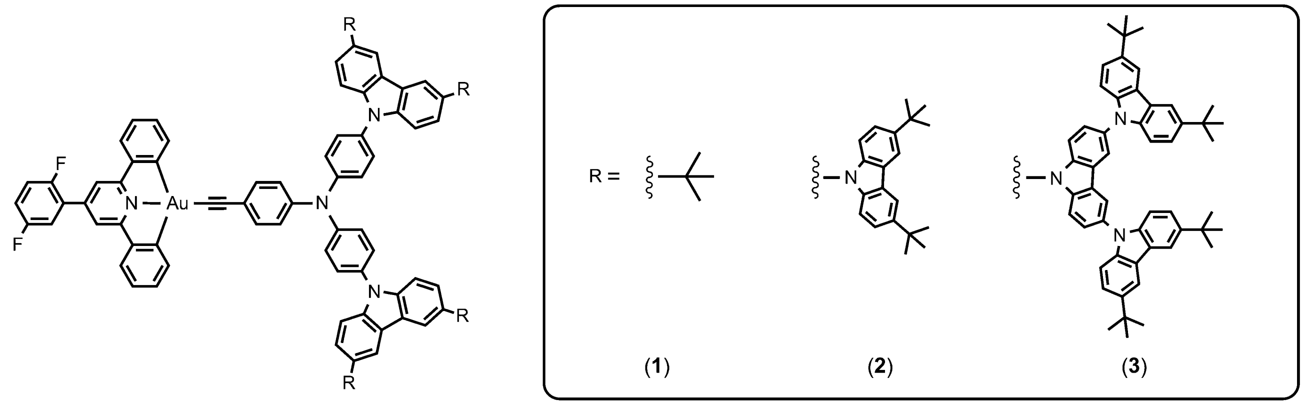

Scheme 1. Chemical structures of the alkynylgold(III) dendrimers **1**–**3**.

Excitation at $\lambda = 380$ nm of solutions of **1**–**3** in dichloromethane at 298 K result in broad structureless emission bands at approximately 620–695 nm (see Figure S2 in the Supporting Information). It is noteworthy that the incorporation of more carbazole units in the higher generation dendrimers would cause a blue shift in energy, that is, **1** (695 nm) < **2** (646 nm) < **3** (620 nm). The lower-lying HOMO energy in the higher generation dendrimers has been attributed to the electron-withdrawing nature of the carbazole dendron, through a negative inductive effect of the electronegative nitrogen atom. Similar electronic effects of the carbazole dendrons in higher generation dendrimers have also been reported by Albrecht and Yamamoto.[11] Such an emission trend is consistent with the reduction potentials for the first oxidation [**1** (+0.94 V versus the saturated calomel electrode (SCE)), **2** (+1.05 V versus SCE), and **3** (+1.12 V versus SCE)] observed in the electrochemical study (see below). As a consequence of the lack of vibronic structures and the presence of the electron-donating triphenylamine substituent on the alkynyltriarylamine ligands, the origin of the emission band of **1**–**3** has been tentatively assigned as derived from an excited state of ^{3}LLCT π[alkynyltriarylamine$\rightarrow\pi^*$[2,5-F_2–C_6H_3–C^N^C] origin.[9] In solid-state thin films, **1**–**3** also display low-energy structureless emission bands, while the emission energies are found to be dependent on the concentration of the dopant in polymethylmethacrylate (PMMA). A red-shift of 1010 cm^{-1} in the emission energies has been observed in the concentration range of 2 to 50 wt% of **1** in PMMA (see Figure S3 in the Supporting Information). Similar to the structurally related gold(III) compounds, such a concentration-dependent behavior may probably be due to excimeric emission in the thin film arising from the π-π stacking of the 2,5-F_2–C_6H_3–C^N^C ligand.[9d] As the dendron generation increases, smaller shifts in the emission energies for **2** (661 cm^{-1}) and **3** (376 cm^{-1}) are observed as the dopant concentration is increased. These findings suggest that the increase in the dendrimer generations effectively alters the degree of intermolecular interactions, and hence leads to a fine-tuning of the emission color.[12]

A quasireversible reduction couple at −1.32 V versus SCE, and an irreversible first oxidation wave at +0.83, +0.94, and +1.06 V versus SCE are found in the cyclic voltammograms of **1**–**3**, respectively, in dichloromethane (0.1 mol dm^{-3} $n$$Bu_4NPF_6$). The photophysical and electrochemical data of **1**–**3** are summarized in Table S1 (see the Supporting Information). The reduction process is assigned as a ligand-centered reduction, while the first oxidation wave of **1**–**3** is attributed to an alkynyl-ligand-centered oxidation.[9b–d] The occurrence of multiple oxidations at higher potential is probably due to oxidations of carbazole moieties, similar to other carbazole-based dendritic iridium(III) complexes.[7b,13]

To study the applicability of dendrimers **1**–**3** as solution-processable electrophosphorescent dopants for the fabrication of PHOLEDs, devices with the configuration of indium-tin oxide (ITO)/poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS; 70 nm)/x% dendrimer:*N*,*N'*-dicarbazolyl-3,5-benzene (MCP; 60 nm)/tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane (3TPYMB) (5 nm)/1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB; 30 nm)/LiF (0.8 nm)/Al (100 nm) have been prepared, in which 3TPYMB and TmPyPB are used as the hole-blocking and electron-transporting layers, respectively. The emissive layer was prepared by spin-coating a solution of dendrimer:MCP blend at different concentrations in dichloromethane. Figure 1 depicts the normalized electroluminescence (EL) spectra of PHOLEDs at a current density of 20 mA cm^{-2}. The EL spectra for all the devices are almost identical to their phosphorescence (PL) spectra without any undesirable emission coming from the adjacent hole- or electron-transporting layers. This confirms that efficient energy transfer between the dendrimers and MCP takes place as a result of the effective confinements of both the charge carriers and triplet excitons. This could further be supported by the alignment of the triplet-state energies (E_T) of the dendrimers and MCP. An E_T value of 2.30 eV for **1**–**3** has been determined from the PL spectra measured at 77 K. As MCP has an E_T value of 2.90 eV, an efficient exothermic energy transfer from the MCP triplet state to the triplet state of the dendrimers would occur, given the perfect E_T alignment. In addition, a red-shift in the emission is observed with increasing dopant concentration, in good agreement with the results from the PL studies. The emission wavelengths are found to shift from 540 to 580 nm in the concentration range of 5 to 50 wt% in MCP, while the Commission Internationale de L'Eclairage (CIE) coordinates

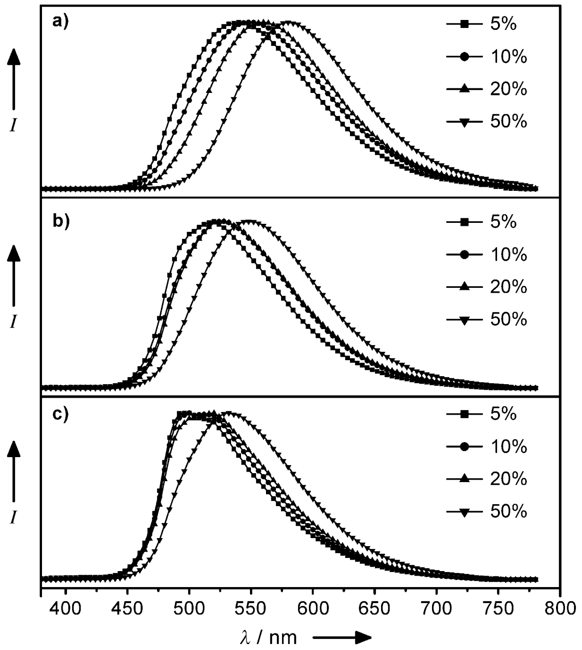

Figure 1. Normalized EL spectra of devices with a) **1**, b) **2**, and c) **3** doped into MCP as the light-emitting layer.

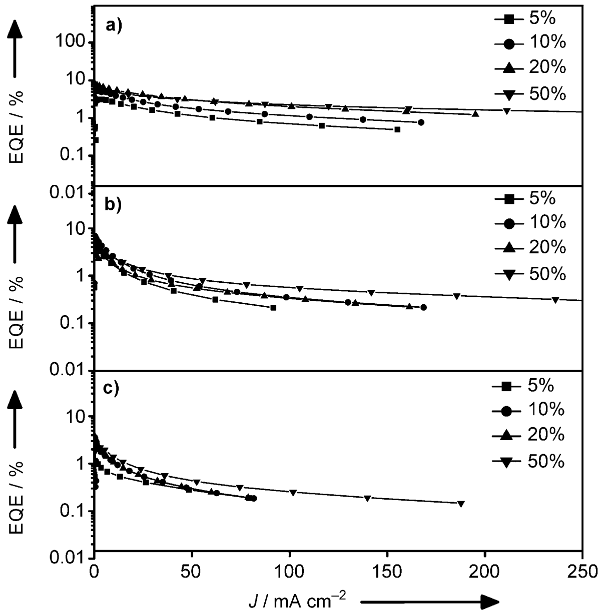

Figure 2. EQE of the devices with a) **1**, b) **2**, and c) **3** doped into MCP as the light-emitting layer.

are found to shift from (0.37, 0.54) to (0.50, 0.49) for the device made with **1**. This concentration dependence could be ascribed to the excimeric emission resulting from π-stacking of the cyclometalated ligand and a better packing of molecules at higher concentrations, which is typically observed in square-planar metal complexes. It is noteworthy that the device made with **2** (or with **3**) shows a reduced bathochromic shift from 520 to 548 nm (or from 500 to 532 nm) upon increasing the dopant concentration. This observation suggests that the intermolecular interactions could be controlled effectively by introducing higher-generation carbazole-based dendrimers to the alkynyltriarylamine ligand.

All the devices have been found to show a promising performance (see Table S2 in the Supporting Information). In particular, a maximum current efficiency of 24.0 cd A^{-1} and a power efficiency of 14.5 Lm W^{-1} can be achieved with the optimized device derived from **1**. These values correspond to a maximum EQE of 7.8 % at a current density of 0.1 mA cm^{-2} (Figure 2 a). Surprisingly, the second generation dendrimer did not result in the degredation of the device performance. The device made with **2** shows maximum current and power efficiencies of 21.9 cd A^{-1} (corresponding to an EQE of 7.0 %) and 16.4 Lm W^{-1}, respectively (see Figure 2 b). This is not the case for other iridium(III) dendrimers, where a poorer performance has been commonly observed for devices made with higher generation dendrimers.[14] This phenomenon can be attributed in these cases to the substantially reduced carrier mobility in higher generation dendrimers. On the other hand, the peak EQE of the device made with **2** is found to drop by only about 10 % compared to that of the device made with **1**. Further introduction of carbazole dendrons to the phosphorescent core to form third generation dendrimer **3** has been found to lower the device performance (i.e. 11.4 cd A^{-1}, 9.6 Lm W^{-1}, and 3.8 %; see Figure 2 c). However, the charge transport ability is improved, as evident from the lower driving voltage of the 50 wt % device with **3** (ca. 7.8 V) at a current density of 20 mA cm^{-2}, relative to that of the 50 wt % device with **1** (ca. 8.2 V). This observation implies that the peripheral carbazole moieties could be actively involved in the charge-transport process. These findings clearly demonstrate that the present dendrimers are potential candidates as phosphorescent dopants for solution-processed light-emitting devices.

In conclusion, a new class of solution-processable dendrimers containing phosphorescent alkynylgold(III) complexes for PHOLEDs has been successfully prepared. The incorporation of carbazole moieties into the phosphorescent core to form higher generation dendrimers has been shown to control the intermolecular interactions effectively as well as to reduce the bathochromic shift of the emission. A superior device performance with maximum current and power efficiencies of 24.0 cd A^{-1} and 14.5 Lm W^{-1} has been achieved for devices employing first generation dendrimers. This corresponds to a high EQE of 7.8 % at a current density of 0.1 mA cm^{-2}. These results suggest that this class of gold(III) dendritic complexes may serve as promising candidates for the fabrication of high-performance solution-processable PHOLEDs.

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