Macromolecules

Dendron-Jacketed Electrophosphorescent Copolymers: Improved Efficiency and Tunable Emission Color by Partial Energy Transfer

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ABSTRACT: A styrene-based phosphorescent monomer VC3DbmIr(ppy)₂ with cyclometalated iridium complex was synthesized. It was then copolymerized with the first-generation dendritic carbazole monomer VC3CbzG1 through the conventional free radical polymerization to obtain a series of electrophosphorescent random copolymers. Characteristic vibrational bands in the FT-IR spectra were utilized to determine the compositions of the copolymers. The glass transition temperatures of the copolymers were about 90 °C, and the 5% weight loss temperatures were all above 346 °C. All the copolymers ex-



hibited similar absorbing bands of the carbazole units in the UV—vis absorption spectra. In the photoluminescent spectra of the copolymer films, energy transfer was found from the carbazole units to iridium phosphors. No obvious energy transfer was found in the copolymer solutions. Light-emitting diodes were fabricated with two configurations. With increasing iridium content, the electroluminescence of the copolymers shifted from blue to orange and passed through a near-white emission region. After the optimization of the device structure, the device containing the copolymer PCbzG1Ir3 had the best performance with a maximum luminescence of 2441 cd/m^2 and a maximum external quantum efficiency of 0.520%.

■ INTRODUCTION

Electrophosphorescent materials utilize both singlet and triplet excitons to emit light, and using these materials can greatly improve the device efficiencies with a 100% internal quantum efficiency in theory.^{1,2} Therefore, electrophosphorescent lightemitting diodes have attracted more and more attention since they were reported in 1998.³ When an organic molecule is excited by an electric field, it can generate a singlet exciting state (S_1) and a triplet exciting state (T_1) , which correspond to the fluorescence and phosphorescence emissions, respectively. In S₁ the electron-spin direction does not change, while in T₁ it reverses. Thus, T₁ is usually difficult to form in an excited molecule because of the spin-forbidden rule. However, in some heavy metal complexes, such as those of Ru, Re, Os, Ir, and Pt, 4,5 T₁ can form under an electric field because of the strong spin-orbit coupling effect. When a complex is excited, the exciting state of the ligand converts into the "metal-to-ligand charge transfer" (¹MLCT) exciting state by the internal conversion. Then ¹MLCT converts into ³MLCT by intersystem crossing due to the overlapping of their potential energy curves. Finally, phosphorescence emits in the radiative transition process of a triplet ³MLCT exciting state.⁶

Electrophosphorescent materials can be classified as small molecules, polymers, and dendritic materials.^{2,7,8} Small-molecular phosphorescent materials are usually doped into a host material in a device to prevent the concentration quenching. The vacuum deposition technique is the main approach to obtain uniform thin films for small-molecular material systems. Phosphorescent

polymers can be processed by spin-coating or inkjet-printing techniques to realize the flexible and large-area displays. Meanwhile, the covalent bonding between a host polymer and a guest molecule can prevent potential phase separation in a doping system.⁹ Furthermore, by introducing different kinds of functional units into a polymer chain, single-layer devices can be acquired.^{10,11} A lot of dendritic materials have also been designed recently to control the intra- or intermolecular interactions. The strong steric hindrance effect is of benefit to inhibit the triplet annihilation.

Dendronized polymers are a special kind of macromolecules,^{12–14} in which dendritic side groups are attached to a linear polymer chain. They can be synthesized by the "graft through", "graft onto", or "graft from" strategies.^{15,16} By increasing the generation of dendritic side groups, the conformation of a polymer can change from a flexible chain to a rigid chain through a semirigid chain. This "jacketing effect" also exists in the mesogen-jacketed liquid crystalline polymers (MJLCPs).^{17–19} In our previous work, we introduced the first- and secondgeneration dendritic carbazole side groups into the MJLCPs system. The two dendron-jacketed polymers, PCbzG1 and PCbzG2, form hexatic columnar nematic phase and columnar nematic phase, respectively.²⁰ The ordered structures of the polymer chains can inhibit the aggregation of intramolecular functional

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Scheme 1. Synthesis Route of VC3DbmIr(ppy)₂



units. The carbazole units are distributed at the surface of the stiff molecular chain, which can provide a continuous carriertransporting channel and favor the light-emitting process.

Dendronized electrophosphorescent polymers have been reported recently.^{21,22} Conventional free radical polymerization and ring-opening metathesis polymerization (ROMP) were utilized to synthesize two kinds of homopolymers containing an iridium complex in the core of the dendritic side group. No obvious decrease of the fluorescence quantum yield was found even with high iridium content, which reflected the isolation effect of the dendritic structure. The other achievement of their work was that compared with the corresponding dendritic monomers, this dendronized structure could greatly improve the solution viscosity, resulting in better film qualities. However, an additional host material was needed for these polymers.

Cyclometalated iridium complexes have been widely used in phosphorescent light-emitting devices because of their high quantum yields and relatively short exiting lifetime.^{2,8} The wavelength of the emitting light can be adjusted by changing the ligand structure.¹ In this contribution, a series of electrophosphorescent random copolymers were synthesized using the dendron-jacketed polymer PCbzG1 as the host material because the first-generation polymer had higher efficiencies and better electroluminescent properties.²⁰ A new monomer containing a cyclometalated iridium complex was synthesized and used as the guest material. The copolymers were used as the emitting layer in the devices without any other host materials. The dendritic side group could isolate the triplet exciton, and the stiff molecular conformation could reduce the intramolecular interaction of the side groups. Furthermore, a wavelength-tunable system was obtained by the intermolecular energy transfer.

EXPERIMENTAL DETAILS

Materials. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol and dried at ambient temperature. Chlorobenzene was washed with sulfuric acid, saturated sodium bicarbonate solution, and water, and it was then distilled under reduced pressure. Tetrahydrofuran (THF) was refluxed with CaH₂ for 8 h and then distilled. All the other reagents were used as received.

Characterization. All of the characterization methods such as ¹H NMR spectroscopy, mass spectrometry, elemental analysis, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), absorption spectra, photoluminescent (PL) spectra, and cyclic voltammetric (CV) analysis used in this study were similar to those reported previously.²⁰

Synthesis. Synthesis of the monomer VC3DbmIr(ppy)₂ was performed as illustrated in Scheme 1. VC3CbzG1 had been synthesized before.²⁰

Synthesis of 1-(4-Hydroxyphenyl)-3-phenylpropane-1,3dione (1). After sodium hydride (2.3 g, 70%, 66.0 mmol) was added into a three-necked flask, a solution of 1-(4-hydroxyphenyl)ethanone (3.0 g, 22.0 mmol) in THF was added dropwise in an ice/water bath with magnetic stirring. The mixture was heated slowly to reflux under a nitrogen atmosphere. After 1 h, methyl benzoate (3.6 g, 26.0 mmol) was added, and the mixture was refluxed for 12 h. After cooled, the mixture was acidified in an ice/water bath. Then THF was removed by a rotary evaporator. The residue was extracted with 50 mL of ethyl acetate and washed with saturated sodium bicarbonate solution and water in

Chart 1. Chemical Structures of the Dendron-Jacketed Electrophosphorescent Copolymers



sequence. After removal of ethyl acetate, the residue was washed with CH_2Cl_2 to obtain the pure product as a yellow solid in 85% yield. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 6.79 (s, 1H, CH₂), 6.90–6.94 (d, 2H, Ar–H), 7.48–7.55 (m, 3H, Ar–H), 7.92–7.99 (m, 4H, Ar–H). MS (HR–ESI): m/z 263.06751 [M + Na]⁺. Anal. Calcd for $C_{15}H_{12}O_3$: C 74.99, H 5.03. Found: C 74.81, H 5.23.

Synthesis of 1-[4-(3-Hydroxypropoxy)phenyl]-3-phenylpropane-1,3-dione (2). 1-(4-Hydroxyphenyl)-3-phenylpropane-1,3dione (2.0 g, 8.3 mmol), 3-bromopropan-1-ol (1.4 g, 10.0 mmol), and potassium carbonate (1.7 g, 12.5 mmol) were added into 100 mL of acetone, and the mixture was refluxed overnight. The hot mixture was filtrated, and the solvent in the filtrate was evaporated by a rotary evaporator. The residue was dissolved in 50 mL of ethyl acetate and washed with a saturated sodium chloride solution (50 mL \times 3). The pure product was obtained by silica gel column chromatography (CH₂Cl₂:ethyl acetate = 15:1, v:v) as a white solid in 72% yield. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.77 (br, 1H, -OH), 2.05-2.11 (m, 2H, CH₂CH₂CH₂), 3.84-3.89 (t, 2H, HOCH₂), 4.16-4.21 (t, 2H, CH₂O), 6.79 (s, 1H, CH₂), 6.92-6.99 (d, 2H, Ar-H), 7.46-7.58(m, 3H, Ar-H), 7.96-8.02 (m, 4H, Ar-H), 16.99 (br, 1H, CH₂). MS (HR-ESI): *m*/*z* 321.10973 [M + Na]⁺. Anal. Calcd for C₁₈H₁₈O₄: C 72.47, H 6.08. Found: C 72.30, H 6.10.

Synthesis of Bis{3-[4-(3-oxo-3-phenylpropanoyl)phenoxy]propyl}-2-vinylterephthalate (3). 2-Vinylterephthalic acid (1.4 g, 7.4 mmol), 1-[4-(3-hydroxypropoxy)phenyl]-3-phenylpropane-1,3dione (4.9 g, 16.3 mmol), N,N'-dicyclohexylcarbodiimide (DCC, 3.9 g, 18.6 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.2 g, 1.8 mmol) were added into 80 mL of CH₂Cl₂. The mixture was stirred for 8 h at ambient temperature and filtrated. The filtrate was concentrated by a rotary evaporator. The residue was washed with acetone first and then purified through a silica gel column using CH2Cl2 as eluent to afford the pure product as a white solid in 75% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 2.27-2.35 (m, 2H, CH₂CH₂CH₂), 4.18-4.22 (m, 2H, CH₂O), 4.54-4.59 (m, 2H, COOCH₂), 5.38-5.41 (d, 1H, CH₂=), 5.71-5.75 $(d, 1H, CH_2 =), 6.79 (s, 1H, CH_2), 6.92 - 6.98 (d, 4H Ar - H), 7.36 - 7.43$ (q, 1H, Ar–H), 7.45–7.55 (m, 6H, Ar–H), 7.89–8.01 (m, 10H, Ar–H), 8.23 (s, 1H, Ar-H), 17.00 (br, 1H, CH₂). MS (LR-ESI): m/z 753.0 [M]⁺. Anal. Calcd for C₄₆H₄₀O₁₀: C 73.39, H 5.36. Found: C 73.31, H 5.37.





Synthesis of the Chloro-Bridged Iridium Dimer $[Ir(ppy)_2-\mu$ -Cl]₂ (4). Iridium chloride trihydrate (1.0 g, 2.8 mmol) and 2-phenylpyridine (1.2 g, 7.8 mmol) were added into a mixed solvent of 2-ethoxyethanol (24 mL) and deionized water (8 mL). The mixture was refluxed at 130 °C for 24 h. Then the precipitate was filtrated and washed with deionized water, acetone, ethanol, and hexane in sequence to afford the crude product as a yellow powder, which was used directly in the following reaction after dried in a vacuum oven.

Synthesis of VC3Dbmlr(ppy)₂ (5). Bis{3-[4-(3-oxo-3-phenylpropanoyl)phenoxy]propyl} (381.8 mg, 0.5 mmol), $[Ir(ppy)_{2^-}\mu$ -Cl]₂ (706.6 mg, 0.7 mmol), and anhydrous sodium carbonate (537.4 mg, 5.1 mmol) were added into 60 mL of acetonitrile. After being stirred at 80 °C for 48 h under a nitrogen atmosphere, the mixture was filtrated, and the filtrate was concentrated by a rotary evaporator. The residue was passed through a silica gel column (petroleum:acetone = 3:2, v:v) to afford the pure product as a red powder in 65% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 2.17–2.16 (m, 2H, CH₂CH₂CH₂), 4.07–4.11 (m, 2H, CH₂O), 4.48–4.53 (m, 2H, COOCH₂), 5.33–5.36 (d, 1H, CH₂=), 5.66–5.71 (d, 1H, CH₂=), 6.35–6.37 (d, 4H, Ar–H), 6.53 (s, 2H, CH₂), 6.70–6.86 (m, 12H Ar–H), 6.96–7.01 (m, 4H, Ar–H), 7.27–7.38 (m, 7H, Ar–H), 7.55–7.65 (m, 8H, Ar–H), 7.78–7.90 (m, 14H, Ar–H), 8.19 (s, 1H, Ar–H), 8.54–8.58 (q, 4H, Ar–H). MS

	iridium content (mol %)						
copolymer	in feed	in copolymer ^{<i>a</i>}	yield (%)	$M_{\rm n}~({ m g/mol})^b$	$M_{\rm w}/M_{\rm n}^{\ b}$	$T_{\rm d}$ (°C) ^c	$T_{g} (^{\circ}C)^{d}$
PCbzG1	0	0	76	52 000	2.01	368	88
PCbzG1Ir05	0.5		79	51 000	2.04	373	88
PCbzG1Ir1	1.0		70	58 000	1.91	356	89
PCbzG1Ir3	3.0	2.1	81	51 000	1.96	352	89
PCbzG1Ir5	5.0	4.0	75	49 000	2.05	347	91
PCbzG1Ir7	7.0	5.6	78	50 000	2.01	352	92
PCbzG1Ir10	10.0	9.2	78	53 000	1.99	346	94

Table 1.	Composition, Mo	lecular Weight,	Molecular W	Veight Distributi	on, and Therma	l Properties of	the Cope	lymers
				<i>a</i>	/			/

^{*a*} Determined by the characteristic absorbing bands in FT-IR spectra. ^{*b*} Determined by GPC in THF using polystyrene standards. ^{*c*} 5% weight loss temperatures determined by TGA at a heating rate of 20 °C under a nitrogen atmosphere. ^{*d*} Evaluated by DSC during the second heating cycle at a rate of 20 °C/min.



Figure 2. TGA (a) and DSC (b) curves of the copolymers.

(MALDI–TOF): m/z 1752.6 [M]⁺. Anal. Calcd for C₉₀H₇₂O₁₀N₄Ir₂: C 61.70; H 4.03; N 3.20. Found: C 61.29; H 4.29; N 3.30.

Copolymer Synthesis. A series of random copolymers PCbzG1*co*-PDbmIr(ppy)₂ (Chart 1) were synthesized from the corresponding styrene-based monomers VC3DbmIr(ppy)₂ and VC3CbzG1. The copolymers were named according to the iridium contents as PCbzG1, PCbzG1Ir05, PCbzG1Ir1, PCbzG1Ir3, PCbzG1Ir5, PCbzG1Ir7, and PCbzG1Ir10. Take the synthesis of PCbzG1Ir10 as an example to illustrate the polymerization process. VC3CbzG1 (200 mg), VC3DbmIr-(ppy)₂ (26.5 mg), chlorobenzene (2.0 g), and 50 μ L of a chlorobenzene solution containing 0.5 mg of AIBN were transferred into a precleaned glass tube. After three freeze—pump—thaw cycles, the tube was sealed off under vacuum. The polymerization was performed at 60 °C for 24 h, and then the reaction was quenched in liquid nitrogen. The tube was opened, and the solution was diluted with 5 mL of THF. The target polymer was precipitated in 200 mL of acetone. To eliminate the unreacted



Figure 3. UV-vis spectra of VC3DbmIr(ppy)₂ and PL spectra of PCbzG1 in THF (a) and films (b).

monomers, the precipitation process was repeated three times. After filtrated and dried, the target copolymer was obtained.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Copolymers. In order to synthesize the target phosphorescent monomer, a β -diketone ligand 1 was synthesized by the Claisen condensation reaction. Excess sodium hydride was used in this reaction because of the existence of the phenolic hydroxyl group. Then a Williamson etherification reaction was performed to synthesize compound 2. The amount of 3-bromopropan-1-ol was in slight excess to avoid the side reaction between the bromine and methylene group in



Figure 4. UV-vis spectra of the copolymers in THF (a) and films (b).

compound 1. An esterification reaction was followed to obtain compound 3. Finally, the coordination reaction was carried out in acetonitrile at 80 °C to afford the target monomer in a relatively high yield.²³ Compound 4 was synthesized according to the reported method.⁸

All of the copolymers were synthesized under similar conditions by the conventional free radical polymerization in chlorobenzene using AIBN as the initiator. The unreacted monomers could be easily removed in the precipitation process because both monomers could be readily dissolved in acetone. FT-IR spectra (Figure 1) of these copolymers were used to determine the compositions of the copolymers and the differences between the real iridium contents and those in feed. With increasing iridium content in feed, the intensity of the characteristic vibrational absorbing bands of C=N in VC3DbmIr(ppy)₂ at 1540 cm⁻¹ increased. According to the Lambert-Beer law, the concentration of functional groups is proportional to the absorbing intensity. On the other hand, the characteristic band of 1,3,5-trisubstituted phenyl in VC3CbzG1 at 1600 cm^{-1} could be chosen as the internal reference to calculate the real iridium content. After the determination of the relationship between the molar ratio of the two monomers and the ratio of the areas of the characteristic bands, the compositions of the copolymers were obtained. The results are summarized in Table 1. For the copolymer PCbzG1Ir05 and PCbzG1Ir1, the compositions were difficult to calculate because the iridium contents were so low that the characteristic bands of C=N could not be observed in the FT-IR spectra. For the other copolymers, the real iridium contents were a little lower than those in feed, which was probably due to the steric hindrance effect of the dendritic side groups in the copolymerization.



Figure 5. PL spectra of the copolymers in THF (0.1 mg/mL) (a) and films (b).

The number-average molecular weights (M_n) 's) of the copolymers, the polydispersity indexes, and the thermal properties are also summarized in Table 1. The M_n 's were all about 50 000 g/mol, and the polydispersity indexes were \sim 2.00. All the copolymerizations afforded high yields of more than 70%. These results indicated that the iridium feed ratio played a minor role on the polymerization process. In the two monomers, a short spacer of three methylene units was introduced into the molecules between the polymerizable sites and the side groups. This special design was based on three reasons. First, an introduction of a flexible spacer could reduce the huge steric hindrance of the dendritic side groups during the polymerization. Second, the spacer decoupled the polymerizable sites and the side groups,⁹ resulting in similar polymerization reactivities for the two monomers, which benefited the synthesis of random copolymers instead of homopolymers or block copolymers. Third, if the dendritic side groups were attached to the main chain of some conjugated polymers, the flexible spacer could inhibit the energy back-transfer.^{23,24} The polymerization results in Table 1 suggest that the flexible spacer was indeed effective in these aspects.

The TGA and DSC curves of the copolymers are shown in Figure 2. The 5% weight loss temperatures $(T_d \cdot s)$ of the copolymers were all above 346 °C (Figure 2a), and only one weight loss step was found in each TGA curve, implying good thermal stabilities, which was in favor of device fabrication. The glass transition temperatures $(T_g \cdot s)$ were ~90 °C. No other phase transitions were found in the DSC curves (Figure 2b). With increasing iridium contents, a small increase in T_g was also found probably because there were less flexible units in the phosphorescent monomer.

Photophysical Properties. In order to prevent the triplet annihilation caused by the high current density or the high concentration of triplet excitons, an effective way is to build up the host—guest system. Guest materials are attached to the host polymers by covalent bonds, and the phosphorescent emission is



Figure 6. Cyclic voltammogram of VC3Dbm(ppy)₂.



Figure 7. Energy level diagram of the materials used in this study.

produced by the energy transfer between the host and the guest or by the carrier-trapping mechanism. For an efficient Förster energy transfer, the degree of overlapping between the PL spectrum of the host and the UV—vis absorption spectrum of the guest is of great importance.^{25,26} Therefore, in the present work, the PL spectrum of PCbzG1 and the UV—vis absorption spectrum of VC3DbmIr-(ppy)₂ were measured. The results of THF solutions and films are shown in Figures 3a and 3b, respectively.

Whether in solutions or in films, the MLCT absorbing bands of the iridium complex were all observed. The singlet ¹MLCT



Figure 9. EL spectra (a) and CIE coordinate (b) of the copolymers.



Figure 8. Device configuration and auxiliary materials used in this study.

Table 2. EL Properties of Device a

samples	U_{onset} (V) ^a	$L_{\rm max}~({\rm cd/m^2})^b$	$\eta_{\mathrm{I,max}}(\mathrm{cd/A})^{c}$	$\eta_{ m L,max}(m lm/W)^d$	$\eta_{\mathrm{ext,max}} (\%)^e$	CIE coordinate ^f	$\lambda \ (nm)^g$
PCbzG1	4.5	635	0.122	0.062	0.119	(0.18, 0.16)	428, 483
PCbzG1Ir1	4.8	639	0.117	0.067	0.079	(0.20, 0.23)	429, 495
PCbzG1Ir3	4.6	680	0.134	0.079	0.060	(0.24, 0.37)	439, 503
PCbzG1Ir5	5.0	1522	0.281	0.116	0.101	(0.37, 0.51)	430, 524
PCbzG1Ir7	5.5	1150	0.140	0.057	0.050	(0.41, 0.52)	432, 565
PCbzG1Ir10	5.3	2096	0.211	0.083	0.058	(0.47, 0.50)	576

^{*a*} Turn-on voltage at 1 cd/m². ^{*b*} Maximum luminance. ^{*c*} Maximum current efficiency. ^{*d*} Maximum luminescence efficiency. ^{*c*} Maximum etternal quantum efficiency. ^{*f*} 1931 CIE coordinate. ^{*g*} Emission wavelength at 6 V.

Table 3. EL Properties of Device b

samples	$U_{\rm onset} ({ m V})^a$	$L_{\rm max}({\rm cd/m^2})^b$	$\eta_{\mathrm{I,max}}(\mathrm{cd/A})^c$	$\eta_{ m L,max}(m lm/W)^d$	$\eta_{\mathrm{ext,max}} (\%)^e$	CIE coordinate ^f
PCbzG1	6.1	1132	0.191	0.093	0.186	(0.18, 0.16)
PCbzG1Ir1	6.7	1613	0.694	0.323	0.467	(0.20, 0.23)
PCbzG1Ir3	6.6	2441	0.880	0.409	0.520	(0.24, 0.37)
PCbzG1Ir5	6.2	3044	0.783	0.394	0.280	(0.37, 0.51)
PCbzG1Ir7	7.4	2257	0.350	0.147	0.126	(0.41, 0.52)
PCbzG1Ir10	7.4	2693	0.413	0.173	0.160	(0.47, 0.50)
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"Turn-on voltage at 1 cd/m². "Maximum luminance. "Maximum current efficiency. "Maximum luminescence efficiency. "Maximum external quantum efficiency. ^f 1931 CIE coordinate.

absorption was at about 400 nm, and the triplet one, ³MLCT, was at about 465 nm.⁸ The two characteristic absorbing bands were effectively overlapped with the emission band of PCbzG1, which provided a necessary condition for the energy transfer from PCbzG1 to the iridium complex. Therefore, it was possible to synthesize electrophosphorescent copolymers using PCbzG1 as the host material.

The UV—vis absorption spectra of the copolymers in THF and films are shown in Figure 4. All the copolymers exhibited similar absorbing bands as PCbzG1 in solutions and films. Only the characteristic bands of the carbazole units were observed in the spectra. The absorption of the iridium complex was not clearly observed, which was probably due to its low content. In addition, the energy of the coordination bond was lower, and its absorption was mainly centered in the infrared region.

The PL spectra of these copolymers in solutions and films were quite different (Figure 5). In THF solutions, all the copolymers exhibited similar emitting bands as PCbzG1. Their peak emissions were all centered at about 440 nm, indicating that the efficient energy transfer from PCbzG1 to the iridium complex did not take place. In contrast, in films, with increasing iridium content, the peak emission of the host became weaker, while a new emission at about 550 nm appeared, with its intensity increasing gradually, which suggested the energy transfer occurred in these films. Compared with the peak emission of the host material in solutions, a 10 nm blue shift was also found in films, which agreed with the results we reported previously.²⁰

For the Förster energy transfer process, a certain distance between the host and the guest is also required in addition to the overlap of their PL and UV—vis absorption spectra. The suitable distance is 5-10 nm. In solutions, the spectra matched well, and both the carbazole and iridium units could readily dissolve. However, the distance between them might exceed the limit, and the energy transfer still could not take place. In films, the molecules were packed more tightly, and carbazole and iridium complexes were close to each other. Therefore, the energy transfer occurred. **Electrochemical Properties.** The electrochemical properties of the host material PCbzG1 had been investigated previously. In this work, the CV behavior of the monomer VC3DbmIr(ppy)₂ was studied, as shown in Figure 6. The onset oxidation potential (0.76 V) and the onset reduction potential (-1.53 V) were obtained directly from the curve, and then the HOMO (-5.11 eV) and LUMO (-2.82 eV) levels were calculated from the equations $E_{\rm HOMO} = -e[U_{\rm onset(ox)} + (4.8 V - U_{1/2,\rm FOC})]$ and $E_{\rm LUMO} = -e[U_{\rm onset(red)} + (4.8 V - U_{1/2,\rm FOC})]$. The energy levels of the materials used in this study are summarized in Figure 7.

As shown in Figure 7, the monomer VC3DbmIr(ppy)₂ possessed a higher HOMO level and a lower LUMO level. Meanwhile, the two levels were in between the corresponding levels of PCbzG1. In this case, the guest played a trapping role, which suggested the possibility of carrier-trapping mechanism in the electroluminescent device based on this guest—host system.

Electroluminescent Properties. The light-emitting devices were fabricated in two configurations (Figure 8) to investigate the electroluminescent properties of the copolymers. Device a had a configuration of ITO/PEDOT:PSS/copolymer/TPBI(15 nm)/ LiF(1 nm)/Al(100 nm) while device b ITO/PEDOT:PSS/copolymer/TPBI(15 nm)/AlQ(30 nm)/Ca(20 nm)/Al(100 nm). The electroluminescent (EL) spectra and the CIE coordinates of the copolymers at 6 V are illustrated in Figure 9.

In Figure 9a, with increasing iridium content of the copolymers, energy transfer from the host to the guest occurred. The blue emission of the host weakened, and the orange emission of the guest gradually increased. Compared with the PL spectra, the energy transfer in the EL spectra was more complete. For the copolymer PCbzG1Ir7 and PCbzG1Ir10, the emission from the host almost disappeared, indicating that the energy transfer tended to be complete. The difference of the PL spectra between the copolymer solutions and the films (Figure 5) had already indicated that the energy transfer might take place in an intermolecular way because no obvious energy transfer was observed in the PL spectra of the copolymer solutions.



Figure 10. Electroluminescent properties of copolymer PCbzG1Ir3 and PCbzG1Ir7 (device b): current density–voltage–luminescence curve (a); current efficiency–current density–power efficiency curve (b); external quantum efficiency–current density curve (c).

When the iridium content was higher, the peak emission of the guest red-shifted to a certain extent. This phenomenon could be attributed to the aggregation of the guest units because the siteisolation effect of the low-generation host polymer PCbzG1 was not strong enough. On the other hand, the intermolecular interactions of the iridium phosphors would also lead to the red shift of the EL spectra. In the CIE coordinate, with increasing iridium content, the emitting color of the copolymers shifted from blue to orange and passed through a near-white region, which suggested that the application of this kind of copolymer might realize the fabrication of a white organic light-emitting diode (WOLED) from a single polymer chain by the intramolecular partial energy transfer. And the emission color could be adjusted by the composition of the copolymer.

The device properties are summarized in Tables 2 and 3. In device b, an electron-transporting layer (8-hydroxyquinoline aluminum, AlQ) was introduced on top of the hole-blocking layer (1,3,5-tri(1-phenyl-1H-benzo[d])imidazol-2-yl)phenyl, TPBI), and then a calcium layer was deposited to enhance the electron-injecting properties. Compared with device a, device b had better overall properties, which could be attributed to the better electron-transporting property of AlQ and improved carrier-transporting balance. With increasing iridium content, the device efficiencies of the two configurations increased first and then dropped. For the optimized device b, the addition of a small amount of iridium complex resulted in a significant improvement of the device performance, which reflected the higher efficiency of the phosphorescent emission.

The device b with the copolymer PCbzG1Ir3 had the best properties. Its luminescence and efficiency curves are shown in Figure 10. The maximum luminescence, current efficiency, and external quantum efficiency were 2441 cd/m², 0.880 cd/A, and 0.520%, respectively. As mentioned above, the generation of the dendritic side group was low. Therefore, the isolation effect for the iridium complex was limited, and the triplet annihilation might still exist to some extent, which led to the decrease of device performance at higher iridium contents. The red-shift of EL spectra at high iridium contents also supported this conjecture.

CONCLUSIONS

In this contribution, a series of electrophosphorescent random copolymers PCbzG1-co-PDbmIr(ppy)₂ were synthesized through the conventional free radical polymerization. The iridium feed ratio played a minor role on the copolymerization process. FT-IR spectra were utilized to determine the compositions of the copolymers, and the real iridium contents were a little lower than those in feed. The copolymers had good thermal stabilities with the 5% weight loss temperatures all above 346 °C. The PL spectrum of PCbzG1 effectively overlapped with the UV-vis absorption spectrum of the iridium monomer, which provided a necessary condition for the energy transfer from the host to the guest. All the copolymers exhibited a single blue emission peak in THF, while in films the energy transfer occurred and the emission from the guest was found. In the EL spectra, more complete energy transfer was observed. With increasing iridium content, the emission color shifted from blue to orange, passing through a near-white region. The emission wavelength could be controlled through the copolymer composition by the intermolecular energy transfer. Two series of electroluminescent devices were fabricated. An introduction of an AlQ layer resulted in better carrier-transporting balance and thus improved the device properties. With increasing iridium content, the device properties passed through a maximum value and then decreased, which was attributed to the limited isolation effect of the dendritic side group. The device b of the copolymer PCbzG1Ir3 had the best performance, with the maximum luminescence, current efficiency, and external quantum efficiency of 2441 cd/m², 0.880 cd/A, and 0.520%, respectively. In order to take full advantage of the site-isolation effect of the dendritic structure, we are currently investigating polymers with dendritic side groups of higher generation and electrophosphorescent dendron-jacketed conjugated polymers.

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