Jacketed Homopolymer with Bipolar Dendritic Side Groups and its Applications in Electroluminescent Devices

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ABSTRACT: A dendritic monomer with bipolar side groups containing dendritic carbazole and oxadiazole structures was synthesized by a convergent strategy. The homopolymer was synthesized through a conventional radical polymerization. The number-average molecular weight determined by gel permeation chromatography was 40,000 g/mol. Its 5% weight loss temperature was 358 °C. Its photophysical properties were studied in solution and in film. The photoluminescent emission peak of the film was at 408 nm, which had a blue shift of 9 nm compared with that of the tetrahydrofuran solution. And there was an energy transfer from oxadiazole to carbazole. The highest occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) levels calculated from cyclic voltammetry data were -5.55 and -2.52 eV, respectively, and the band gap was 3.03 eV, which suggested that the polymer had both hole- and electron-transporting capabilities. The efficiencies of the single-layer device based on this homopolymer were much higher than those of the same-generation homopolymer without the oxadiazole moiety. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 581–589, 2012

KEYWORDS: liquid-crystalline polymers (LCP); phase behavior; supramolecular structures

INTRODUCTION Organic light-emitting diodes (OLEDs) have been intensely researched because of their advantages in applications as flat panel displays and lighting. Organic light-emitting materials can be classified into small molecules, polymers, and dendrimers. Since the first report of high-efficiency small molecular OLED (SMOLED),¹ OLEDs began to attract more and more attention. Compared with SMOLEDs, polymer light-emitting diodes have better thermal stabilities and can be readily processed using various methods, such as spin-coating and inkjet-printing, to achieve flexible and large-area displays.

Polymer light-emitting materials can be divided into the mainchain type and the side-chain type. For the main-chain polymers, the conjugated main chains are synthesized by condensation polymerization, and they are good for carrier injection and transportation.² This kind of rigid structures can suppress the intramolecular interactions. However, the intermolecular aggregation may lead to undesirable changes of emitting colors.^{3,4} The side-chain polymers can be synthesized by conventional radical polymerization or living/controlled radical polymerizations.⁵⁻¹⁰ The molecular weight can be controlled, and the solubility is good. However, the unconjugated backbones, which are nonfunctional and usually flexible, result in relatively poor carrier-transporting ability and device efficiencies. Dendrimers have well-defined core-shell structures, good solubility, low viscosity, and very large shell surface with many functional groups.¹¹ Unlike common polymers, dendrimers always have exact molecular weights, monodispersity, and definite structures. They can also be processed by solution-based techniques for polymers. Recently, dendronized polymers, the combination of linear polymers and dendrimers, have also attracted intensive interests.¹²⁻¹⁴ Some dendronized polymers with conjugated^{15,16} or unconjugated¹⁷⁻¹⁹ backbone have been synthesized. They can self-assemable into different interesting architectures.

Polymers dendronized with twin-dendritic side groups can self-organize into liquid crystalline phases.^{20–22} Recently, we reported a new class of electroluminescent dendronized polymer with twin-dendritic carbazole side groups.²³ The dendritic side groups force the main chain to take a rigid, extended conformation, and the first- and second-generation polymers assemble into columnar phases. This kind of structures can suppress the intramolecular interactions and formation of excimers, which benefit the optoelectronic properties.^{24,25}

For an efficient OLED, the balanced hole and electron transporting capabilities are important. However, common molecules usually have single transporting ability, holes or electrons. There are several ways to balance the transportation

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of holes and electrons. The first way is to build up multilayer devices. The disadvantage is the tedious device fabrication. The second way is doping. Although the manufacturing is relatively easy, it may suffer from several problems such as phase separation and crystallization. The third way is to introduce both hole- and electron-transporting moieties into the same molecule, which has the so-called bipolar structure.^{26,27} Carbazole units are well known for their holetransporting properties,^{23,28} while oxadiazole derivatives are efficient electron-transporting and hole-blocking materials.^{29,30} The combination of these two moieties can prospectively lead to the improvement of electroluminescent properties. Copolymers and homopolymers can both be synthesized as bipolar polymers. Bipolar copolymers from N-vinylcarbazole and oxadiazole-containing monomers have been synthesized.^{24,31} However, the reactivities of different monomers vary, and their contents in the polymers are different from those expected. As a result, the compositions and structures are not well controllable. For a homopolymer, the ratio of the functional groups can be precisely controlled because each repeat unit has the same structure. Thus, we expect to obtain a homopolymer with a bipolar structure. We can also change the diameter of the rod-like polymer chain by changing the generation of the dendritic side groups. In addition, we can obtain polymer chains with different lengths by controlling the degree of polymerization. Furthermore, this kind of Janus dendritic monomer makes it possible to control the structures and properties by changing its dendrons.^{32,33} By adjusting the generations of different carrier moieties, the carrier-transporting balance will be improved.

In this contribution, we report the synthesis of a homopolymer from a dendritic monomer with bipolar side groups containing dendritic carbazole and oxadiazole structures. Its application in electroluminescent diode is also discussed.

EXPERIMENTAL

Device Fabrication and Characterizations

The device fabrication process used and the characterization methods such as gel permeation chromatography (GPC), ¹H NMR spectroscopy, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-vis spectrum, photoluminescent (PL) spectrum, and cyclic voltammetry (CV) were similar to those we used previously.²³

Materials

2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Chlorobenzene was washed with sulfuric acid and then distilled under reduced pressure. Bis[3-(9*H*-carbazol-9yl)propyl]-5-(3-hydroxypropoxy)-isophthalate (HC3CbzG1), 5-(benzyloxy)isophthalic acid, and 4-(octyloxy)benzohydrazide were obtained as reported before.^{23,34} All the other reagents were used as received.

Synthesis

The synthetic routes are outlined in Scheme 1.

Synthesis of BnOXDG1 (3)

5-(Benzyloxy)isophthalic acid (3.8 g, 13.9 mmol) was dissolved in SOCl₂ (50 mL), then five drops of N,N'-dimethylfor-

mamide (DMF) was added. The reaction mixture was refluxed for 3 h. After cooled to ambient temperature, the excess SOCl₂ was removed by a rotary evaporator to give a white powder 1, which was then dissolved in CH_2Cl_2 (100 mL) and added dropwise to a solution of 4-(octyloxy)benzohydrazide (8.0 g, 30.3 mmol) and triethylamine (30 mL) in CH₂Cl₂ (100 mL) in an ice/water bath. The yellow solution was subsequently stirred at ambient temperature for 8 h, and the mixture was condensed by a rotary evaporator at 50 °C to give a crude product of 2, which was dissolved in POCl₃ (150 mL) directly and heated to reflux for 12 h. The color of the reaction solution changed from yellow to orange-red gradually and finally to dark brown. After cooled to ambient temperature, it was poured into stirring ice/ water (2000 mL) slowly. The brown precipitate was filtered and washed with water until the filtrate was neutral. The filtrate cake was dissolved in a small amount of CH_2Cl_2 and subjected to silica gel column chromatography (CH₂Cl₂:EtOAc = 20:1) to give a white solid (6.0 g, 8.2 mmol) in 60% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.88–0.92 (t, 6H, CH₃), 1.31-1.35 (m, 16H, CH₂), 1.45-1.49 (m,4H, OCH₂CH₂CH₂), 1.79-1.86 (m, 4H, OCH₂CH₂), 4.02-4.06 (t, 4H, OCH₂), 5.25 (s, 2H, OCH₂), 7.02-7.04 (d, 4H, Ar-H), 7.35-7.39 (t, 1H, Ar-H), 7.42-7.46 (t, 2H, Ar-H), 7.51-7.53 (d, 2H, Ar-H), 7.88-7.90 (d, 2H, Ar-H), and 8.08-8.10 (d, 4H, Ar-H). MS (LR-ESI): m/z 728.4 [M+H]⁺. Anal. Calcd. for C₄₅H₅₂N₄O₅: C, 74.15; H, 7.19; N, 7.69. Found: C, 74.20; H, 7.19; N, 7.68.

Synthesis of HC3OXDG1 (4)

BnOXD-G1 (6.0 g, 8.2 mmol) was dissolved in tetrahydrofuran (THF) (250 mL), and Pa/C catalyst (2.0 g) was added. The mixture was stirred under a hydrogen atmosphere in water bath at 40 °C for 8 h. 3-Bromopropan-1-ol (2.3 g, 16.5 mmol), anhydrous potassium carbonate (2.3 g, 16.5 mmol), potassium iodide (0.3 g, 2.0 mmol), and acetonitrile (150 mL) was added in the reaction mixture simultaneously. The mixture was heated to reflux overnight. After cooled to ambient temperature, the mixture was filtered through celite. The filtrate was concentrated. The residue was first washed with acetone, and the pure product was obtained by silica gel column chromatography (CH_2Cl_2 :EtOAc = 4:1) as a white solid (5.0 g, 7.5 mmol) in 90% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.89-0.92 (t, 6H, CH₃), 1.31-1.36 (m, 16H, CH₂), 1.44-1.52 (m,4H, OCH₂CH₂CH₂), 1.75–1.82 (m, 4H, OCH₂CH₂), 2.12-2.17 (m, 2H, OCH2CH2), 3.95-4.01 (m. 6H, OCH2), 4.27-4.30 (t, 2H, HOCH₂), 6.97-6.99 (d, 4H, Ar-H), 7.61 (s, 2H, Ar-H), 7.99-8.02 (d, 4H, Ar-H), and 8.32 (s, 1H, Ar-H). MS (LR-ESI): *m*/*z* 697.4 [M+H]⁺, 719.4 [M+Na]⁺. Anal. Calcd. For C₄₁H₅₂N₄O₆: C, 70.66; H, 7.52; N, 8.04. Found: C, 70.64; H, 7.54; N, 8.02.

Synthesis of BnCbzCOOH (5)

5-(Benzyloxy)isophthalic acid (4.5 g, 16.5 mmol) was dissolved in SOCl₂ (80 mL), and then five drops of DMF was added. The reaction mixture was refluxed for 3 h. After cooled to ambient temperature, the excess SOCl₂ was removed by a rotary evaporator. The white residue was dissolved in dry CH_2Cl_2 (100 mL), which was added with a solution of HC3CbzG1 (4.4 g, 6.7 mmol) and triethylamine



SCHEME 1 Synthetic routes of the monomer and the polymer.

(30 mL) in CH_2Cl_2 (100 mL) in an ice/water bath. The mixture was stirred at ambient temperature for 8 h and then for an additional 30 min after water (100 mL) was added. The organic layer was separated, dried with anhydrous magnesium sulfate, and then concentrated with a rotary evaporator. The crude product was purified by silica gel column chromatography (CH₂Cl₂:EtOH = 20:1) to give a white solid (5.8 g, 6.4 mmol) in 95% yield. ¹H NMR (400 MHz, DMSO, δ , ppm): 2.24–2.29 (m, 6H, COO CH₂CH₂CH₂O, COO CH₂CH₂CH₂N), 4.21–4.27 (m, 6H, CH₂O, CH₂N), 4.51–4.57 (m, 6H, COO CH₂), 5.16 (s, 2H, OCH₂), 7.12–7.16 (t, 4H, Ar—H), 7.29–7.42 (m, 9H, Ar—H), 7.51 (s, 2H, Ar—H), 7.57–7.59 (d, 4H, Ar—H),

7.73 (s, 2H, Ar—H), 7.94 (s, 1H, Ar—H), and 8.08–8.11 (m, 5H, Ar—H). MS (LR-ESI): m/z 909.3 [M+H]⁺, 931.3 [M+Na]⁺. Anal. Calcd. For C₅₆H₄₈N₂O₁₀: C, 73.99; H, 5.32; N, 3.08. Found: C, 73.55; H, 5.42; N, 3.13.

Synthesis of BnCbzOXD (6)

BnCbzCOOH (5.6 g, 6.2 mmol), HC3OXDG1 (4, 4.3 g, 6.2 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide mmol), hydrochloride (EDC·HCl, 1.7 g, 8.9 mmol), and 4-dimethylamino pyridine (DMAP, 0.2 g, 1.6 mmol) were added into CH₂Cl₂ (200 mL), and the mixture was stirred at ambient temperature for 5 h. The solvent was removed by a rotary evaporator. The residue was dissolved in EtOAc (300 mL), washed with saturated sodium chloride solution (3 \times 100 mL), and dried with anhydrous magnesium sulfate. Then, the solvent was removed by a rotary evaporator, and the residue was purified through a silica gel column (CH_2Cl_2 :EtOAc = 20:1) to give a pale yellow solid (8.4 g, 5.3 mmol) in 85% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.88–0.91 (t, 6H, CH₃), 1.25-1.40 (m, 16H, CH₂), 1.46-1.48 (m,4H, OCH₂CH₂CH₂), 1.78-1.85 (m, 4H, OCH₂CH₂), 2.33-2.38 (m, 8H, COO CH₂CH₂CH₂O, COO CH₂CH₂CH₂N), 4.01-4.03 (t, 4H, OCH₂), 4.19–4.21 (t, 2H, OCH₂), 4.26–4.29 (t, 2H, OCH₂), 4.31-4.34 (t, 4H, NCH₂), 4.46-4.49 (t, 4H, COOCH₂), 4.55-4.59 (t, 4H, COOCH₂), 5.07 (s, 2H, OCH₂), 7.00-7.02 (d, 4H, Ar-H), 7.16-7.20 (m, 4H, Ar-H), 7.29-7.41 (m, 13H, Ar-H), 7.69-7.70 (d, 2H, Ar-H), 7.70-7.81 (m, 4H, Ar-H), 8.04-8.08 (m, 8H, Ar-H), 8.29-8.30 (m, 2H, Ar-H), and 8.36 (s, 1H, Ar—H). MS (LR-ESI): m/z 1588.7 [M+H]⁺, 1610.7 $[M+Na]^+$, 1626.7 $[M+K]^+$. Anal. Calcd. For $C_{97}H_{98}N_6O_{15}$: C, 73.37; H, 6.22; N, 5.29. Found: C, 73.21; H, 6.32; N, 5.23.

Synthesis of HC6CbzOXD (7)

BnCbzOXD (6, 8.4 g, 5.3 mmol) was dissolved in THF (250 mL), and Pa/C catalyst (1.5 g) was added. The mixture was stirred under a hydrogen atmosphere in water bath at 40 °C for 8 h. 6-Bromohexan-1-ol (3.0 g, 16.6 mmol), anhydrous potassium carbonate (3.0 g, 21.7 mmol), potassium iodide (0.2 g, 1.2 mmol), and acetonitrile (150 mL) was added in the reaction mixture, which was heated to reflux overnight. After cooled to ambient temperature, the mixture was filtered through celite. The filtrate was vacuumed to remove the solvent. The residue was dissolved in a small amount of CH₂Cl₂ and purified through a silica gel column (CH₂Cl₂: EtOAc = 5:1) to give a white solid (6.3 g, 3.9 mmol) in 74% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.88–0.91 (t, 6H, CH₃), 1.30-1.48 (m, 24H, CH₂), 1.55-1.58 (m, 2H, HOCH₂CH₂), 1.74-1.85 (m, 6H, OCH₂CH₂), 2.32-2.38 (m, 8H, COO CH₂CH₂CH₂O, COO CH₂CH₂CH₂N), 3.61-3.64 (t, 2H, HOCH₂), 3.95-3.98 (t, 2H, OCH₂), 4.01-4.04 (t, 4H, OCH₂), 4.19-4.22 (t, 2H, OCH2), 4.27-4.30 (t, 2H, OCH2), 4.32-4.35 (t, 4H, NCH₂), 4.46-4.50 (t, 4H, COOCH₂), 4.56-4.59 (t, 4H, COOCH₂), 7.00-7.03 (d, 4H, Ar-H), 7.16-7.20 (m, 4H, Ar-H), 7.37-7.42 (m, 8H, Ar-H), 7.69-7.70 (m, 8H, Ar-H), 7.76-7.77 (d, 2H, Ar-H), 8.04-8.08 (m, 8H, Ar-H), 8.27-8.29 (m, 2H, Ar-H), and 8.35 (s, 1H, Ar-H). MS (LR-ESI): m/z 1598.8 [M+H]⁺. Anal. Calcd. For C₉₆H₁₀₄N₆O₁₆: C, 72.16; H, 6.56; N, 5.26. Found: C, 71.96; H, 6.59; N, 5.22.

Synthesis of VC6CbzOXD (8)

2-Vinylterephthalic acid (0.3 g, 1.6 mmol), HC6CbzOXD (7, 5.5 g, 3.4 mmol), EDC·HCl (1.3 g, 6.8 mmol), and DMAP (0.1 g, 0.8 mmol) were added into CHCl₃ (150 mL), and the mixture was stirred at ambient temperature for 5 h. The reaction solution was washed with saturated sodium chloride solution (3 \times 100 mL) and dried with anhydrous magnesium sulfate. Then, CHCl₃ was removed by a rotary evaporator. The pure product was obtained through silica gel column chromatography (CH_2Cl_2 :EtOAc = 15:1) as a white solid (0.7g, 0.2 mmol) in 15% yield. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.88-0.98 (t, 12H, CH₃), 1.26-1.35 (m, 32H, CH₂), 1.35-1.54 (m, 16H, HOCH₂CH₂), 1.76-1.83 (m, 16H, HOCH₂CH₂), 3.95-4.03 (m, 12H, OCH₂), 2.33-2.37 (m, 16H, COOCH₂CH₂CH₂O, COO CH₂CH₂CH₂N), 4.18-4.21 (t, 4H, OCH₂), 4.27-4.34 (m, 16H, NCH₂), 4.45-4.49 (t, 8H, COOCH₂), 4.55-4.57 (t, 8H, COOCH₂), 5.37-5.40 (d, 1H, =CH₂), 5.70-5.74 (d, 1H, =CH₂), 7.00-7.02 (d, 8H, Ar-H), 7.15-7.19 (m, 8H, Ar-H), 7.38-7.43 (m, 17H, Ar-H, =CH), 7.68-7.70 (m, 8H, Ar-H), 7.75-7.76 (d, 4H, Ar-H), 7.85-7.93 (m, 2H, Ar-H), 8.03-8.07 (m, 16H, Ar-H), 8.2 (d, 1H, Ar-H), 8.27-8.28 (m,4H, Ar-H), and 8.34 (s, 2H, Ar-H). MS (MALDI*m/z* 3375.5 $[M+Na]^+$. Anal. TOF): Calcd. For $C_{202}H_{212}N_{12}O_{34}$: C, 72.38; H, 6.37; N, 5.01. Found: C, 72.47; H, 6.56; N, 4.85.

Polymerization

VC6CbzOXD (500 mg), chlorobenzene (1.89 g), and AIBN (98 μ L, 5 mg/mL in chlorobenzene) were transferred into a glass tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was performed at 60 °C for 24 h, and the mixture was quenched in liquid nitrogen. Then, the tube was opened. The white polymer was obtained through silica gel column chromatography in 20% yield using CH₂Cl₂ as eluent. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.75–2.26 (m, CH₂CH₂, CH₃), 3.36–4.51 (m, OCH₂, NCH₂), and 6.31–8.12 (m, Ar—H).

RESULTS AND DISCUSSION

Synthesis

There are three strategies to synthesize a dendronized polymer, "graft-through," "graft-onto," and "graft-from." The "graftthrough" strategy is to polymerize a dendritic macromonomer which was synthesized first.35,36 The "graft-onto" strategy is to perform a reaction between a dendrimer and a polymer chain.^{37,38} The "graft-from" strategy is to synthesize a polymer chain with initiating sites and then initiate the growth of the dendrimer generation by generation.39,40 We chose the "graft-through" strategy to synthesize the target dendronized polymer because the structure of the polymer would be precise with a 100% grafting density. The core of the target dendritic monomer contained a vinyl, which would easily undergo some side reactions during a long synthetic route. Therefore, we chose a convergent method to synthesize the dendritic shell first and then introduce the vinyl into the molecule in the last step.

To obtain a dendritic monomer with a high yield, a high-efficiency "protection-deprotection" reaction is of great **TABLE 1** Molecular Weight Information and Thermal Properties

 of the Polymer

Yield (%)	<i>M</i> _n (g/mol) ^a	PDI ^a	$T_{d} (^{\circ}C)^{b}$	7 _g (°C)⁰
30	40,000	1.33	358	59

^a Determined by GPC using polystyrene standards.

 $^{\rm b}$ 5% weight loss temperature determined by TGA under a nitrogen atmosphere at a heating rate of 20 $^\circ{\rm C/min}.$

 $^{\circ}$ Determined by DSC in the second heating process at a heating rate of 20 $^{\circ}\text{C/min}.$

importance. In the present work, a hydrogenation reaction of benzyl in the presence of Pd/C catalyst was chosen. In the hydrogenation reaction of BnOXDG1, the reaction mixture obtained was gel-like, leading to a tedious purification process. This phenomenon was probably caused by the strong hydrogen-bonding interaction between the oxadiazole moiety and the phenolic hydroxyl. When the mixture was heated, the hydrogen bond was destroyed, and HOXDG1 became soluble in THF. Therefore, HOXDG1 was not purified, and the reaction mixture was used directly in the following etherification reaction. A small amount of CH_3CN was added into the mixture to increase the polarity of the solution, which was good for the nucleophilic substitution. The similar process was performed when hydrogenating BnCbzOXD.

To obtain BnCbzCOOH (5) with a high yield, 5-(benzyloxy)isophthalic acid should be much excess compared with HC3CbzG1. However, in an esterification reaction using *N*,*N'*dicyclohexylcarbodiimide as dehydrating agent, the poor solubility of 5-(benzyloxy)isophthalic acid led to a very low concentration of carboxyl group in solution and resulted in a heterogeneous reaction. Both of the two carboxyl groups would react with the hydroxyl group. Because 5-(benzyloxy)isophthaloyl dichloride (1) could dissolve readily in CH_2Cl_2 and THF, with the excess amount of 1, 5 with the asymmetric structure could be synthesized, and the high yield of over 90% demonstrated that this method was highly efficient.

The number-average molecular weight (M_n) , polydispersity index (PDI), and thermal properties of the polymer are summarized in Table 1. The GPC curve is shown in Figure 1, and the TGA and DSC traces are shown in Figure 2. The molar ratio of monomer to initiator in the polymerization was 50:1. However, the degree of polymerization calculated from M_n was about 12. The difference between the designed degree of polymerization and the real one was probably due to the inaccurate molecular weight determined by GPC. A dendronized polymer usually has a smaller hydrodynamic volume than that of a linear polymer with the same molecular weight. Therefore, the GPC method might underestimate the molecular weight of the dendronized polymer.

The relatively high PDI could be attributed to the conventional polymerization method. The high T_d indicated that the polymer had a good thermal stability. However, the T_g was relatively low, probably caused by the flexible alkyl tails and spacers in the molecule. We chose octyls as the tails because the very bad solubility of BnOXDG1 with shorter tails



FIGURE 1 GPC curve using polystyrene as standards.

resulted in almost no reduction during hydrogenation. The polymer had good solubility in organic solvents, such as CH_2Cl_2 , THF, and chlorobenzene.

Photophysical Properties

The absorption and emission data are summarized in Table 2. The UV-vis absorption of the polymer in THF solution and



FIGURE 2 TGA (a: at a heating rate of 20 °C/min) and DSC (b: at a heating rate of 20 °C/min) traces of the polymer.

TABLE 2 UV-vis and PL Spectra Data in Solution and in Film

In TH	C	lo fi	m
UV (nm) ^a	PL (nm) ^{b,c}	UV (nm) ^d	PL (nm) ^{c,e}
261, 295, 310	417	261, 296, 311	408

^a 10⁻⁵ mol/L.

^b 0.1 mg/mL.

^c Excitation wavelength was 310 nm.

 $^{\rm d}$ The film was spin-coated from a THF solution (10 mg/mL) and dried at ambient temperature.

 $^{\rm e}$ The film was cast from a THF solution (10 mg/mL) and dried at ambient temperature.

in film was investigated. The concentration of the solution was about 10^{-5} mol/L, and the film was fabricated on a quartz substrate by spin-coating from a THF solution (10 mg/mL). The spectra are shown in Figure 3. The absorption peaks at about 260 and 295 nm were attributed to the carbazole segments.²³ The shoulder peaks at about 310 nm was caused by the oxadiazole segments.²⁴ The onset absorptions at 353 nm in solution and 359 nm in film gave the calculated band gaps of 3.51 and 3.46 eV, respectively.

The PL emission spectra excited at 310 nm both in solution and in film were also measured. The concentration of the solution was 0.1 mg/mL, and the film was cast from a THF solution (10 mg/mL). The spectra are shown in Figure 4. The emission peak in THF was 417 nm. In film, the emission peak was 408 nm, a blue shift of 9 nm compared with that in THF. This phenomenon might be attributed to the rearrangement of the polymer chains in film.²³ To verify which part of the polymer emitted the light, we investigated the PL emissions of the intermediates, HC3CbzG1 and HC3OXDG1, in film. For HC3OXDG1, the main emission peak was at 375 nm, and there was an obvious aggregation peak at about 540 nm. For HC3CbzG1, the main emission peaks were at 414 and 434 nm, and there was a shoulder peak at about 480 nm. In the polymer, there was only one peak at 408 nm, which was very close to that of HC3CbzG1. This indicated



FIGURE 3 Normalized UV-vis absorption spectra in THF and in film.



FIGURE 4 Normalized PL spectra of PCbzOXD in THF and in film (a) and those of HC3CbzG1 and HC3OXDG1 in film (b).

that an energy transfer from the oxadiazole moiety to carbazole moiety occurred. Additionally, the long-wavelength emissions in both HC3CbzG1 and HC3OXDG1 were probably caused by the aggregation of the molecules. This phenomenon was more clearly observed in HC3OXDG1 because it



FIGURE 5 Cyclic voltammogram of the polymer film coated on the carbon electrode.

TABLE 3 Electroluminescent Properties of	of PCbzOXD and PCbzG2
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Device	Polymer	$U_{ m onset}~({ m V})^{ m a}$	$L_{\rm max}~({\rm cd}/{\rm m}^2)^{\rm b}$	η _{Imax} (cd/A) ^c	$\eta_{Lmax} \ (Im/W)^d$	η _{extmax} (%) ^e	CIE Coordinate ^f
а	PCbzG2	7.2	33	0.007	0.003	0.005	0.18, 0.19
а	PCbzOXD	9.0	12	0.042	0.015	0.030	0.18, 0.21
b	PCbzG2	5.0	763	0.093	0.043	0.068	0.18, 0.19
b	PCbzOXD	7.2	184	0.100	0.032	0.069	0.18, 0.21
c	PCbzG2	6.4	1182	0.167	0.063	0.122	0.18, 0.19
C	PCbzOXD	9.1	214	0.115	0.039	0.086	0.18, 0.21

^a Turn-on voltage at 1 cd/m².

^b Maximum luminance.

^c Maximum current efficiency.

^d Maximum luminescence efficiency.

^e Maximum external quantum efficiency.

^f 1931 CIE coordinate.

was a planar molecule and could easily stack through π - π interaction. In contrast, no undesirable long-wavelength emission in the polymer film was observed, which suggested that the huge steric hindrance of the dendritic side group could effectively suppress the aggregation of the functional moieties.

Electrochemical Properties

CV was used to investigate the electrochemical properties of the homopolymer. The result is illustrated in Figure 5. On the anodic sweep, the onset potential was 1.20 V, which was attributed to the oxidation of the carbazole moiety. On the cathodic sweep, the onset potential was -1.83 V, which was attributed to the reduction of the oxadiazole moiety. According to the formulae $E_{\text{HOMO}} = -e[U_{\text{onset(ox)}} + (4.8 \text{ V} - U_{1/2,\text{FOC}})]$ and $E_{LUMO} = -e[U_{onset(red)} + (4.8 \text{ V} - U_{1/2,FOC})]^{23}$ the HOMO and LUMO energy levels were calculated to be -5.55 and -2.52 eV, respectively. By introducing the oxadiazole moieties into the polymer, no significant difference was found in the HOMO level compared with the result we reported previously.23 However, the LUMO level decreased dramatically, owing to the electron affinity of the oxadiazole moiety. This result indicated that the homopolymer had a potential for transporting electrons. The band gap calculated from HOMO and LUMO levels was 3.03 eV, which was significantly different from that calculated from the onset absorption in film (3.46 eV). This large deviation might result from the different testing methods and mechanisms. The onset oxidation or reduction started from part of the side groups, while the UVvis absorption method considered the side groups as a whole. Therefore, the optical band gap would be larger than the electrochemical one.9

Electroluminescent Properties

The light emitting devices were fabricated in three configurations [device **a**, ITO/PEDOT:PSS/Polymer/LiF (1 nm)/Al (90 nm); device **b**, ITO/PEDOT:PSS/Polymer/1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl (TPBI; 15 nm)/Ca (20 nm)/Al (90 nm); device **c**, ITO/PEDOT:PSS/Polymer /TPBI (15 nm)/8-hydroxyquinoline aluminum (AlQ; 30 nm)/Ca (20 nm)/Al (90 nm)]. The results are shown in Table 3.

Figure 6 shows the EL spectrum of device $c\ \text{at}$ 16 V. Its emission peaks were at 450 and 486 nm, both of which

were blue. Compared with the polymer PCbzG2 we reported previously,²³ which only contained carbazole side groups, the EL spectrum of PCbzOXD red-shifted about 15 nm. This was probably caused by the reduction of the band gap because of the reduced LUMO level.

The most important advantage of bipolar molecules is that they perform better in single-layer devices. Therefore, we fabricated devices **a** with PCbzG2 and PCbzOXD. The current efficiency, energy efficiency, and external quantum efficiency of PCbzOXD were one order of magnitude higher than those of PCbzG2. The performance of the device with PCbzOXD was better because its carrier transportation was more balanced than that of PCbzG2.

To optimize the device structure, TPBI was added (device **b**). The device performances were greatly improved, with the corresponding differences between PCbzG2 and PCbzOXD reduced, because TPBI acted as a hole-blocking and electron-transporting layer. On the one hand, it made the recombination of electrons and holes confined in the emitting layer; on the other hand, the electron-transporting capability of the electroluminescent polymers was improved, especially for PCbzG2.

In the further optimization of the device structure, electrontransporting layer AlQ was added (device c). The



FIGURE 6 EL spectrum of device c.

performance of the device with PCbzG2 was greatly improved, while that with PCbzOXD showed less improvement. The maximum current efficiency and energy efficiency were 0.115 cd/A and 0.039 lm/W, respectively. In this device structure, the efficiencies of PCbzOXD were even slightly lower than those of PCbzG2. The addition of AlQ could improve the electron-transporting capability of the device, which was good for PCbzG2. For PCbzOXD, because it already had the electron-transporting moiety oxadiazole, AlQ might break the balance of carrier transportation, resulting in less improvement of device performance.

CONCLUSIONS

A dendritic monomer containing carbazole and oxadiazole moieties was synthesized. And conventional radical polymerization was conducted to obtain a homopolymer with good thermal stability. However, the flexible parts of the molecule led to a low $T_{\rm g}$. Its UV-vis absorption peaks in film were at 261, 296, and 311 nm. The PL emission peak of the film was at 408 nm. And an energy transfer from oxadiazole to carbazole occurred. The PL emission peak in film showed a blue shift of 9 nm compared with that in THF. No undesirable long-wavelength emission was observed because the huge steric hindrance of the dendritic side groups could suppress the aggregation of the molecules. The HOMO and LUMO levels estimated by electrochemistry were -5.55 and -2.52 eV, respectively, with a band gap of 3.03 eV. The single-layer device of the homopolymer PCbzOXD showed much higher efficiencies than those of the second-generation homopolymer PCbzG2 reported previously, which had the same generation as PCbzOXD, indicating the more balanced carrier transportation of the polymer. Device \mathbf{c} showed the best performance with the maximum luminance of 214 cd/m^2 , maximum external efficiency of 0.086%, and maximum current efficiency of 0.115 cd/A.

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