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Zinc Tetraphenylporphyrin−Fluorene Branched Copolymers: Synthesis and Light-Emitting Properties

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ABSTRACT: Three novel branched zinc tetraphenylporphyrin (ZnTPP)−fluorene copolymers **P12**, **P100**, and **P1000**, with different ZnTPP content, were designed and synthesized by a "$A_2 + A_2' + B_4$" approach based on a facile one-pot Suzuki polycondensation reaction. The molar ratio of ZnTPP to fluorene units in the copolymers is 5.50% for **P12**, 0.91% for **P100**, and 0.08% for **P1000**. The copolymers are thermally stable, readily soluble in common organic solvents, and show ZnTPP content-dependent absorption and emission properties. The band gap of the copolymers decreased with increasing content of ZnTPP from **P1000** to **P12**, and the emission color of the copolymers changed from purplish pink to red. The OLED device using **P12** as emitter showed pure red emission (CIE coordinates of $x = 0.64$, $y = 0.30$) with a maximum luminance of 740 cd/m^2, which is among the highest values for pure red light-emission OLEDs based on porphyrin-containing copolymers. It is noteworthy that these devices all show reasonably stable efficiency over a broad current range, which is a satisfactory performance meeting the need for active-matrix-driven devices.

Introduction

Organic light-emitting diodes (OLEDs) and organic/polymeric light-emitting materials have attracted tremendous interest due to their potential application in large area flat-panel displays.[1,2] To achieve full-color displays, three primary colors are required. Short wavelength light-emitting blue fluorescent materials are commonly used as either emitter or host, while green and red fluorescent materials can be used as the emitter or the dopant in the fabrication of OLEDs. Some organic dyes were used as the red emission doping materials.[3] Porphyrin is one kind of the red-emission organic dyes, which exhibits reasonable fluorescence efficiency and good thermal stability. Examples of porphyrins used as red emitting materials include tetraphenylporphyrin (TPP) and porphyrin−platinum(II).[4] However, in the OLED devices based on guest−host doped emitter system, the optimum dopant concentration is usually very low and the effective doping range is very narrow, which are due to the doped red dyes being prone to aggregate in solid film at higher doping concentration, and thus leads to self-quenching of their fluorescence and results in lower efficiency for the devices.[5] In addition, the doped red dyes tend to crystallize, which is also not propitious to high performance light-emitting devices. While at lower doping concentration, the energy transfer from the host materials to the guest (red dyes) is often incomplete, which brings the devices to a poor color purity.[6,7] To overcome above-mentioned problems, some polymers based on porphyrin derivative were investigated.[8,9] But the brightness of devices made from these polymers were generally very low (< 200 cd/m^2) or even not mentioned at all.

Here, we report one kind of zinc tetraphenylporphyrin (ZnTPP)−fluorene branched copolymers, as shown in Scheme 1, which were synthesized by a novel "$A_2 + A_2' + B_4$" approach based on Suzuki coupling method. For getting better red emission, we used ZnTPP instead of free base TPP. The high photoluminescence quantum efficiency oligofluorenes were chosen to harvest energy and transfer it to porphyrins. Using this kind of "$A_2 + A_2' + B_4$" copolymerization method, we can easily adjust the content of porphyrin in a broader composition range and do not influence the molecular weight of the materials significantly at the same time, and thus the emitting color of the copolymers can be changed in a large color range from pink to pure red. Furthermore, compared with linear polymers, the branched polymers could have larger harvest energy section and larger steric hindering effect because of its ball-shaped structure. Larger harvest energy section could lead to more effective energy transfer, and larger steric hindering is favorable of stable glass formation and less prone to self-aggregation in the solid state.[10] The OLED devices results show that the emission color of the three copolymers changed from purplish pink of **P1000** to red of **P12** with the increase of ZnTPP content in the copolymers, which indicates that energy transfer extent from fluorene units to ZnTPP units in these three copolymers were very different. The maximal brightness of the OLEDs reached 740 cd/m^2 for **P12** with pure red emission, 1040 cd/m^2 for **P100** and 2320 cd/m^2 for **P1000**. To the best of our knowledge, the device employing **P12** as emitter demonstrated one of the highest brightness in the pure red emission OLEDs based on the porphyrin derivatives as reported up to now.

Experimental Section

Materials. All reagents and solvents were commercial grade and used without further purification. 2-Bromo-9,9-dioctylfluorene (**5**),[11] 9,9-dioctylfluorene-2-boronic acid (**6**),[12] 2,7-dibromo-9,9-dioctylfluorene (**3**), and 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (**4**)[13] were synthesized by the

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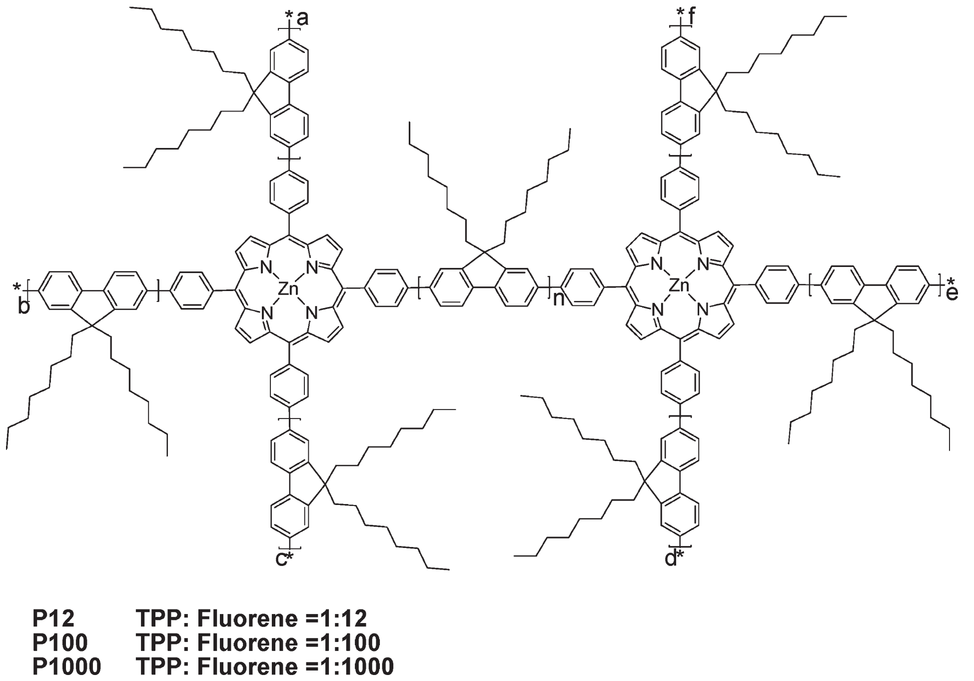
Scheme 1. Molecular Structures of the Copolymers



methods as reported in the corresponding literatures. All reactions were performed under nitrogen atmospheres.

Measurements and Characterization. The gel permeation chromatography (GPC) measurements were performed on a Waters 515-2410 with polystyrenes as reference standard and tetrahydrofuran (THF) as an eluent. The NMR spectra were recorded on a Bruker AV 600 spectrometer in $CDCl_3$ at room temperature. Elemental analyses were performed on a Flash EA 1112 analyzer or Elementar vario EL III. Thermal gravimetric analysis (TGA, Netzsch TG209C) and the differential scanning calorimetry (DSC, TA-Q100) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min. UV−vis absorption spectra were recorded on a Shimadzu spectrometer model UV-3150. Emission spectra were measured at room temperature with a Varian CARY Elipse fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) of the samples in toluene were determined by using ZnTPP (0.033 in toluene) and 1,6-diphenyl-1,3,5-hexatriene (DPH) (0.80 in cyclohexane) as standards. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with a Pt plate, Pt wire, and Ag/Ag^+ electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6)−acetonitrile solution. Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solutions in THF (analytical reagent, 1 mg/mL) on the working electrode and were then dried in air.

Synthesis of the Monomers. *5,10,15,20-Tetra(4-bromophenyl)porphyrin (1).* A solution of 4-bromobenzaldehyde (9.25 g, 50 mmol) in 6 mL of DMSO was added into 120 mL of propionic acid, and then the mixture was stirred and heated to reflux. A mixture of 3.5 mL of pyrrole (50 mmol) and 10 mL of acetic anhydride was added dropwise to the above reaction mixture. The reaction mixture was stirred for 2 h and then cooled to room temperature. The precipitate was collected after filtration and washed with propionic acid. The solid was purified by recrystallization in ethanol to obtain the title compound **1** (2.29 g, 19.7%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.83 (s, 2H), 8.06 (d, 2H), 7.90 (d, 2H), −2.89 (s, 0.5H).

5,10,15,20-Tetra(4-bromophenyl)porphyrin Zinc (**2**). $Zn(OAc)_2 \cdot 2H_2O$ (2.19 g, 10 mmol) was added into a solution of compound **1** (1.75 g, 1.88 mmol) in DMF (150 mL). The reaction mixture was stirred and refluxed for 5 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2/petroleum ether) to afford a purple solid (1.59 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.94 (s, 2H), 8.06 (d, 2H), 7.90 (d, 2H).

Synthesis of the Polymers. The synthesis of the polymers was carried out using palladium-catalyzed Suzuki coupling between monomer 5,10,15,20-tetra(4-bromophenyl)porphyrin zinc (**2**), 2,7-dibromo-9,9-dioctylfluorene (**3**), and 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (**4**), as shown in Scheme 3. All starting materials, reagents, and solvents were carefully purified, and all procedures were performed under an air-free environment.

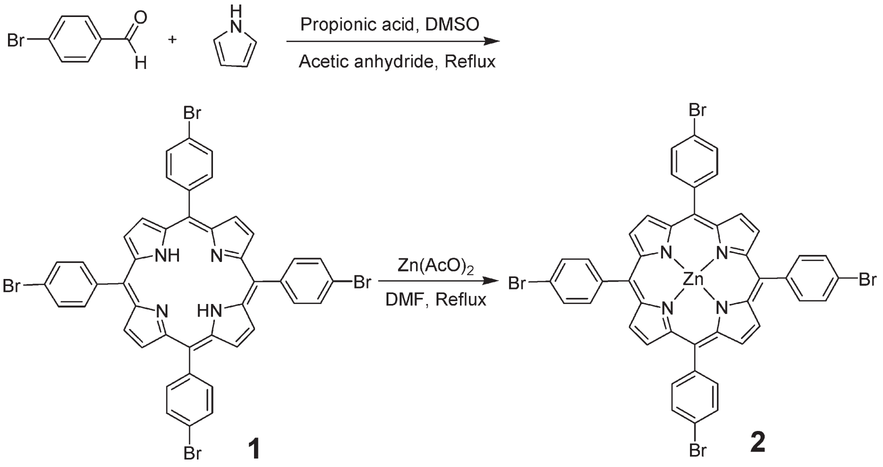
Under the protection of nitrogen, monomers **2**, **3**, and **4** were dissolved in a mixture consisting of toluene, THF, and Na_2CO_3 (2 M). The solution was flushed with nitrogen for 10 min, and $Pd(PPh_3)_4$ (1−2 mol %) was added. After another flushing with nitrogen for 20 min, the reactant was heated to reflux for 12−48 h. The terminal 2-bromo-9,9-dioctylfluorene (**5**) and 9,9-dioctylfluorene-2-boronic acid (**6**) were added as end-cappers, with **5** added first and **6** added 12 h later. After stirring for another 12 h, the reaction solution was cooled to room temperature. The reaction mixture was added dropwise to 200 mL of ethanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with ethanol, hexane, and chloroform. The polymer was recovered as a solid from the chloroform fraction after rotary evaporation. The solid was dried under vacuum. The yields of the polymerization reactions were 37−68%.

P12. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.05−9.25 (broad, 3H), 8.60−8.85 (broad, 21H), 8.38 (broad, 15H), 7.90−8.10 (broad, 33H), 7.83 (broad, 100H), 7.66 (broad, 215H), 2.12 (broad, 201H), 1.54 (broad, 241H), 1.00−1.35 (broad, 1369H), 0.60−1.00 (broad, 612H). GPC: M_n = 25.7K, M_w = 58.6K, PDI = 2.28. Elemental Anal. Found: C: 85.19, H: 9.58, N: 0.84.

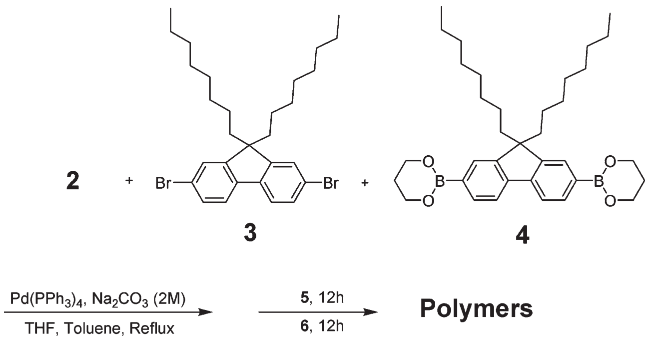
P100. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.10−9.20 (broad, 1H), 8.60−8.85 (broad, 2H), 8.38 (broad, 2H), 7.95−8.20 (broad, 8H), 7.83 (broad, 100H), 7.67 (broad, 217H), 2.12 (broad, 201H), 1.00−1.35 (broad, 1211H), 0.60−1.00 (broad, 570H). GPC: M_n = 19.3K, M_w = 41.4K, PDI = 2.14. Elemental Anal. Found: C: 88.14, H: 10.46, N: 0.13.

P1000. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.83 (broad, 100H), 7.67 (broad, 214H), 2.11 (broad, 201H), 1.00−1.35

Scheme 2. Synthetic Route of 5,10,15,20-Tetra(4-bromophenyl)porphyrin Zinc



Scheme 3. Synthetic Routes of the Copolymers



(broad, 1213H), 0.60−1.00 (broad, 565H). GPC: M_n = 27.0K, M_w = 50.9K, PDI = 1.89. Elemental Anal. Found: C: 88.01, H: 10.49, N: 0.04.

Fabrication and Characterization of the OLED Devices. The device configuration of the OLEDs is ITO/PEDOT:PSS-(30 nm)/PVK-poly-TPD(50 nm)/copolymers(100 nm)/Ca-(10 nm)/Al(100 nm). The ITO-coated glass substrate was cleaned with detergent, then ultrasonicated in acetone and isopropyl alcohol, and subsequently dried in an oven. Then PEDOT:PSS (P-4083, Bayer AG) was spin-casted (2000 rpm) with a thickness of ~30 nm from aqueous solution. The substrate was dried at 150 °C for 30 min in air and then moved into a glovebox for spin-casting the active layers. The binary-host PVK/poly-TPD were dissolved in chlorobenzene and spin-cast on top of the PEDOT:PSS as the HTL (host-transporting layer). The HTL was annealed at 110 °C for 45 min. Then, the solution of the copolymers in toluene was spin-cast on the top of the HTL as the EML (electroluminescent layer). Similarly, the EML was also treated by thermal annealing at 100 °C for 30 min. At last, a layer of Ca capped with Al was thermally deposited through a shade mask at a pressure of ca. 5×10^{-5} Pa. The thickness of the active layer was determined by an Ambios Tech. XP-2 profilometer. The current−voltage ($I-V$) and luminance−voltage ($L-V$) characteristics were conducted on a computer-controlled Keithley 236 source-measure unit and a Keithley 2000 multimeter coupled with a Si photomultiplier tube.

Results and Discussion

Synthesis of Monomers and Polymers. The synthetic routes of the monomers and corresponding polymers are outlined in Schemes 2 and 3, respectively. 5,10,15,20-Tetra-(4-bromophenyl)porphyrin (**1**) was synthesized in about 20% yield by acid-catalyzed condensation of pyrrole with 4-bromobenzaldehyde, followed by oxidation with DMSO at refluxing temperature in one pot, similar to Adler's method.[14] Then porphyrin **1** was treated with zinc acetate, and zinc porphyrin **2** was readily obtained in high yield. Copolymers were prepared by Suzuki coupling reaction[15] and confirmed by ^{1}H NMR spectroscopy and elemental analysis. Based on the elemental analysis, the compositions of three copolymers are in well agreement with the expected results (as shown in Table 1), indicating that the synthetic approach enables the design and adjustment of the porphyrin content in copolymer expediently according to our demand.

All these polymers have good solubility in common organic solvents such as chloroform, THF, and toluene. All the polymers can be readily processed to form smooth and pinhole-free films upon spin-coating. Feed ratio, number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the polymers are shown in Table 1.

Thermal Analysis. The thermal properties of the polymers were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. **P12**, **P100**, and **P1000** have good thermal stability with onset decomposition temperatures with 5% weight loss at 436, 430, and 429 °C, respectively, as shown in Figure 1a. Figure 1b shows DSC traces of the three polymers. Glass transitions were observed at 80−90 °C for the three polymers. **P100** and **P1000** have melting points at 141−145 °C. Although **P12** has no melting point, it has another glass transition point at 160 °C. It is obvious that the T_g of the copolymers was increased after introducing the porphyrin unit, which is possibly due to reduced segmental motions as well as long oligofluorenes chain in the polymers.

Optical Properties. Figure 2 shows the optical properties of the polymers in chloroform solutions and in films on quartz plates. In chloroform solutions, all three polymers exhibited a broad absorption from 300 to 415 nm, which is corresponding to the absorption of the oligofluorene segments. The intensive Soret band at 428 nm and weak Q-bands in the absorption of three polymers are due to the porphyrin segments. Compared with their absorption in the solutions, the Soret bands in the absorption of the polymer films were red-shifted by about 6 nm, and there were only slight broadening peaks, which is due to the aggregation of the porphyrin rings.

The normalized photoluminescent (PL) spectra of the polymers in chloroform solutions and films are shown in

Table 1. Polymerization Results and Characterization of the Copolymers[a]

				elemental analysis:[b] found (wt %)			ZnTPP content (mol %)	
	feed ratio (2:3:4)	M_w	PDI	C	H	N	calculated[c]	found[d]
P12	1:5:7	58.6K	2.28	85.19	9.58	0.84	8.33	5.50
P100	1:49:51	41.4K	2.14	88.14	10.46	0.13	1.00	0.91
P1000	1:499:501	50.9K	1.89	88.01	10.49	0.04	0.10	0.28

[a] Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) determined by means of GPC. [b] Elemental analyses were performed on a Flash EA 1112 analyzer for **P12** and Elementar vario EL III for **P100** and **P1000**. [c] ZnTPP content of the copolymers was calculated from the feed ratio. [d] Actual molar fraction of the ZnTPP unit in the copolymers was determined by elemental analysis (EA).

Table 2. Photophysical Properties of the Copolymers

	λ_{Abs} (nm) (in solution)	λ_{PL} (nm) (in soloution)	λ_{Abs}(nm) (in film)	λ_{PL} (nm) (in film)	Φ_{PL}[a]
P12	384, 429	416, 450, 602, 652	378, 434	617, 668	0.04
P100	388, 427	420, 444	380, 436	440, 467, 610, 662	0.68
P1000	390	423, 444	382, 436	441, 467, 614, 666	0.96

[a] Fluorescence quantum yields (Φ_F) of the copolymers, using ZnTPP as standards for **P12** and 1,6-diphenyl-1,3,5-hexatriene (DPH) for **P100** and **P1000**.

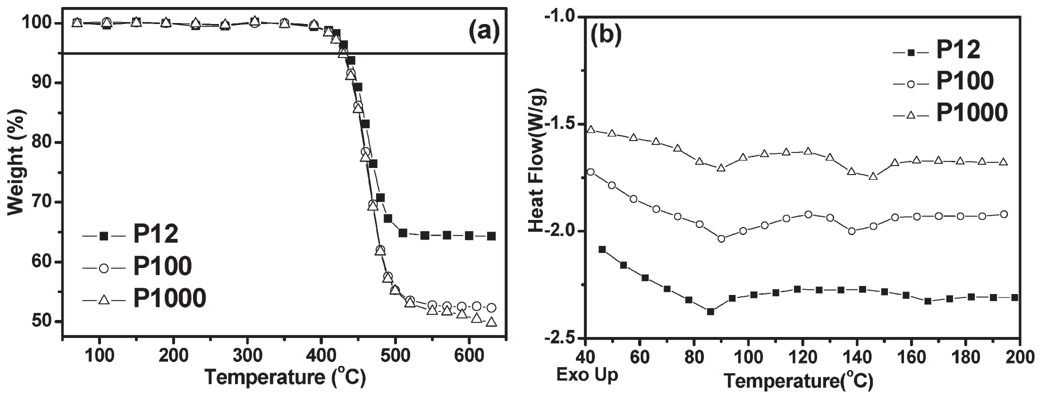


Figure 1. (a) TGA plots of the polymers with a heating rate of 10 °C/min under an inert atmosphere. (b) DSC thermogram of the polymers.

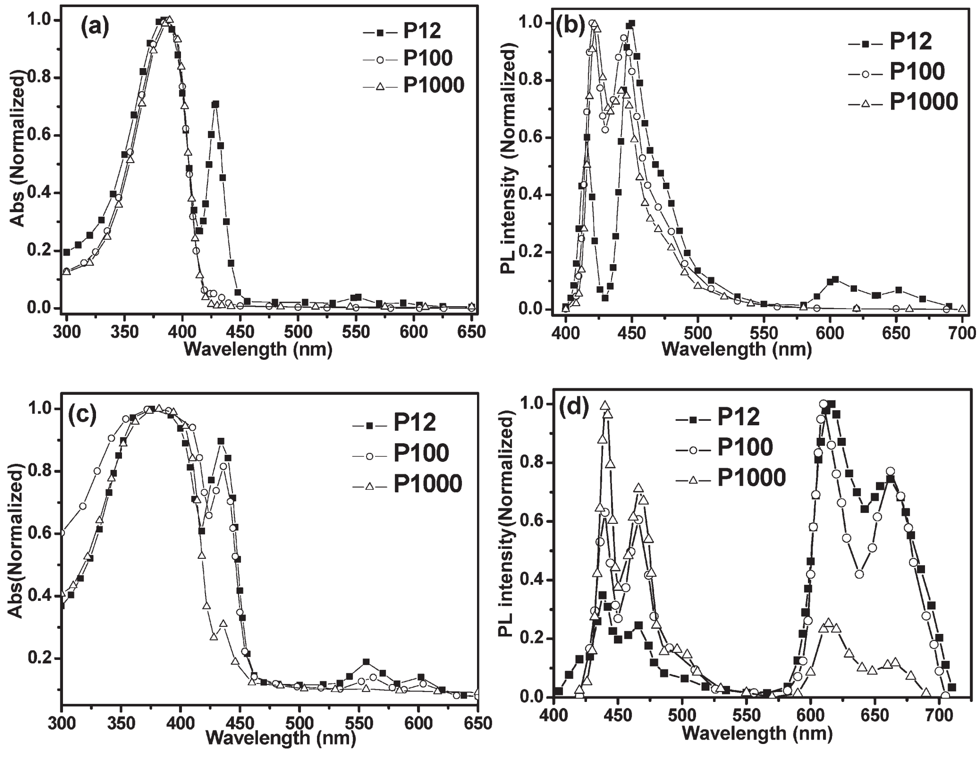


Figure 2. Normalized absorption and PL spectra of the polymers: (a) UV−vis absorption of polymers in chloroform. (b) Photoluminescence spectra of polymers solutions in chloroform (excited at 360 nm). (c) UV−vis absorption of polymers films on quartz plates. (d) Photoluminescence spectra of polymer films on quartz plates (excited at 360 nm).

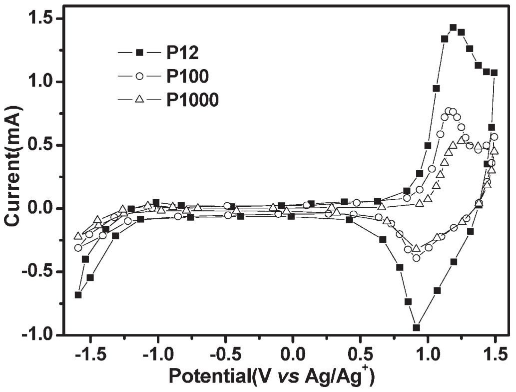


Figure 3. Cyclic voltammograms of the polymer films on Pt electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution with a scan rate of 100 mV/s.

Table 3. Electrochemical Potentials and Band Gaps of the Polymers

	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)[a]
P12	−5.66	−3.58	2.08	2.00
P100	−5.69	−3.50	2.19	2.38
P1000	−5.73	−3.45	2.28	2.78

[a] Optical band gap was obtained from the empirical formula $E_g^{opt} = 1240/\lambda_{edge}$, in which λ_{edge} is the onset wavelength of its absorption peak in the longer wavelength direction.

Figure 2b,d. In solutions, **P12** exhibited emissions both in blue and red regions, but **P100** and **P1000** only exhibited emissions in blue regions. The blue emission is due to the incomplete energy transfer from oligofluorene segments to the porphyrin segment. In films, **P12** displayed an intensive red emission peak at around 617 nm with a shoulder at 670 nm, while the emissions from the oligofluorene segments almost disappeared. **P100** and **P1000** revealed both emission from fluorene segments (400−525 nm) and from the TPP moieties (600−700 nm). The pure red emission of **P12** indicates that the energy transfer in **P12** is more efficient than in **P100** and **P1000**. The more efficient energy transfer in films than that in solutions is probably due to the smaller torsion angle between porphyrin and fluorene,[3] the shorter chromophore distances, and efficient intermolecular exciton mobility in films.[7] The fluorescence quantum yields (Φ_F) of the polymers in dilute chloroform solutions with ZnTPP (Φ_F = 0.033) and 1,6-diphenyl-1,3,5-hexatriene (DPH) (Φ_F = 0.80) as the reference standard were 0.04, 0.68, and 0.96 for **P12**, **P100**, and **P1000**, respectively.

Electrochemical Properties. Cyclic voltammetry has been employed and considered as an effective tool in investigating electrochemical properties of conjugated oligomers and polymers.[16] From the onset oxidation and reduction potentials in the cyclic voltammogram, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be readily estimated, which correspond to ionization potential (IP) and electron affinity (EA), respectively.[17]

Cyclic voltammograms of the polymer films are shown in Figure 3. The HOMO and LUMO energy levels of the polymers are calculated from the onset oxidation potentials and the onset reduction potentials and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc$^+$) to be −4.8 eV below the vacuum level.[18] The formal potential of Fc/Fc$^+$ was measured to be 0.09 V against Ag/Ag$^+$. The results were also listed in Table 3.

The LUMO energy levels of the polymers were estimated to be −3.58, −3.50, and −3.45 eV, respectively. The HOMO energy levels of the polymers are higher than that of polyfluorenes (PFs) (−5.8 eV),[19] which implies a lower barrier for the hole injection in the devices based on the ZnTPP−fluorene copolymers than that in the TPP/PFs-doped systems. ZnTPP molecules have a HOMO−LUMO energy separation smaller than that of PFs, so they could act as efficient charge traps. It has been shown that PFs-based OLEDs are injection limited,[20] and the current flowing through such devices is dominated by holes.[21] The introduction of hole traps would lead to a reduction in the hole current and an enhanced electron injection. The band gaps of the polymers decreased with the increasing of fluorene content. From the HOMO and LUMO energy levels, the band gaps of the copolymers were estimated to be 2.08, 2.19, and 2.28 eV for **P12**, **P100**, and **P1000**, respectively.

Electroluminescent Properties. OLEDs with the configuration of ITO/PEDOT:PSS/PVK+poly-TPD(1:1)/polymer/Ca/Al were fabricated to investigate the electroluminescent (EL) properties of the copolymers. The binary hole-transporting layer of PVK+poly-TPD(1:1) was used to take the advantages of poly-TPD (which can resist the solvent dissolving during the spin-coating of the EML) and PVK (with a higher LUMO level as an electron-blocking material).[22] Figure 4a shows the EL spectra of the polymers, which are very different from the corresponding PL spectra. In EL spectra, the polymers exhibited emissions in a single peak instead of double ones in PL spectra in either blue or red regions. The complete disappearance of the blue emission from the oligofluorene segments indicated that an efficient energy transfer from oligofluorene segments to porphyrin moieties occurred in **P12**. **P100** and **P1000** exhibited emissions in both blue and red regions. More interestingly, **P12** shows a pure red EL peak at 630 nm with a narrow full width at half-maximum (fwhm) of 28 nm. In comparison with the PL spectrum of **P12** film (see Figure 2d), the shoulder peak at 668 nm in the PL did not appear in its EL spectrum, which could be due to different mechanism of the PL and EL. The PL mainly resulted from the energy transfer from oligofluorenes to the porphyrin units, while the EL may result from the charge trapping of the charge injection in the OLEDs.

Figure 4b,c shows the characteristics of luminance and current density versus bias of the OLEDs based on the polymers, and the related EL data are summarized in Table 4. The turn-on voltage (at 1 cd/m^2) of TPP-doped devices increased with the concentration of TPP.[7] But, in this copolymer system, the turn-on voltages of the EL devices are in the range of 7.9−8.2 V, which keeps constant and is much lower than that (ca. 20 V) of the TPP/PFs blend device.[7] The maximal luminance and current efficiency are 740−2320 cd/m^2 and 0.06−0.45 cd/A, respectively. The emission changed gradually with increasing ZnTPP content in the copolymers, from purplish pink to red (Figure 5).

Specifically, the EL spectrum of **P12** peaked at about 630 nm, and the fwhm of the EL peak is very narrow (only 28 nm). The OLEDs using **P12** as emitting material showed pure red emission (CIE coordinates of x = 0.64, y = 0.30) with a luminance of 740 cd/m^2 at a driving voltage of 17.4 V. The brightness of this device is much higher than most of the OLEDs based on porphyrins.[3,8,9,23] It is noteworthy that these devices all show reasonably stable efficiency over a broad current range,[3a,24] as shown in Figure 4d, which is a satisfactory performance meeting the need for active-matrix-driven devices.

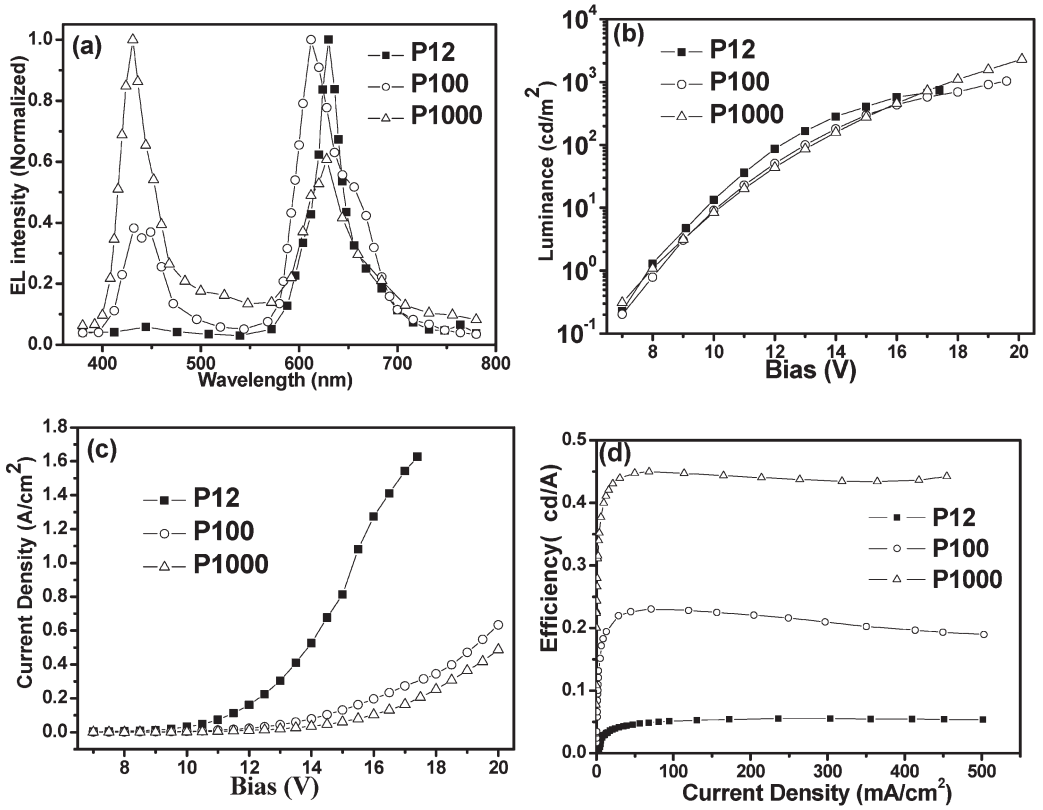


Figure 4. (a) EL spectra, (b) luminance−voltage curves, (c) current density−voltage curves, and (d) efficiency−voltage curves of the OLED devices.

Table 4. EL Properties of the OLEDs

device	V_{on}[a] (V)	L_{max}[b] (cd/m^2)	EL peak wavelength (λ_{em}, nm)	current efficiency (cd/A)[c]	CIE coordinates (x, y)
P12	7.9	740	630	0.06	(0.64, 0.30)
P100	8.2	1040	432, 445, 612, 660	0.23	(0.54, 0.27)
P1000	8.0	2320	431, 630	0.45	(0.41, 0.23)

[a] Turn-on voltage at 1 cd/m^2. [b] Luminance at maximum bias voltage. [c] Maximum current efficiency.

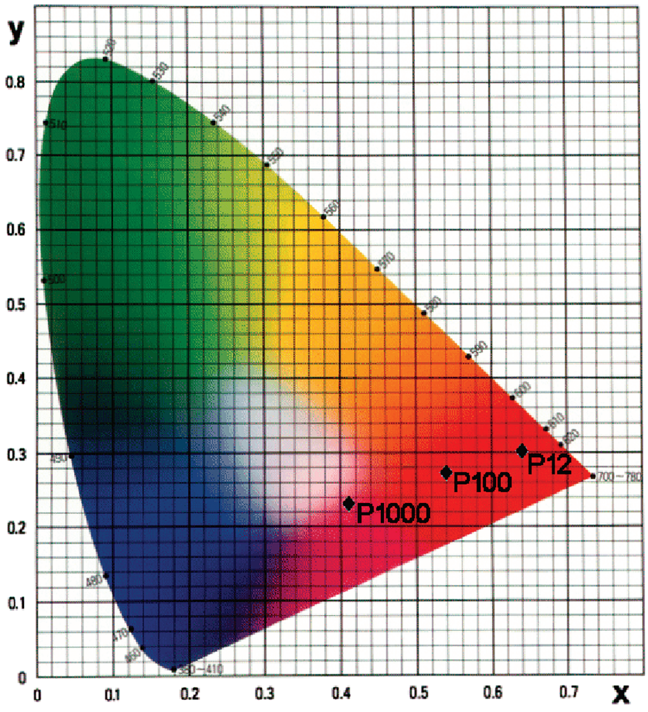


Figure 5. CIE chromaticity coordinates of the OLEDs based on **P12**, **P100**, and **P1000**.

Conclusion

Three copolymers of fluorene and ZnTPP have been successfully synthesized by the palladium-catalyzed one-pot Suzuki coupling reaction. They demonstrated moderate glass transition temperatures (> 80 °C) and good thermal stability (T_d > 420 °C). The EL devices based on the copolymers displayed much lower turn-on voltages and higher luminance than those of the devices based on TPP/PFs. The maximal luminance and current efficiency are 740, 1040, and 2320 cd/m^2 and 0.06, 0.23, and 0.45 cd/A for **P12**, **P100**, and **P1000**, respectively. The EL emission color was gradually changed with the ZnTPP contents in the copolymers, from purplish pink at low content of ZnTPP in **P1000** to pure red at high content of ZnTPP in **P12**. One of the brightest red OLEDs based on porphyrins was achieved using **P12** as emitting material, which showed pure red emission (CIE coordinates of x = 0.64, y = 0.30) with a narrow fwhm (28 nm) of the EL peak and a luminance of 740 cd/m^2 at a driving voltage of 17.4 V. The results reveal that this kind of porphyrin−fluorene branched copolymers would be promising red light-emitting materials. More importantly, this work has developed a novel molecular design toward improving color purity and luminance of the red-light-emitting materials.

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References and Notes

(1) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. B.; Marks, R. N.; Mackay, K.; Friend, R. H.; Bum, P. L.; Holmes, A. B. *Nature* (*London*) **1990**, *347*, 539. (b) Gross, M.; Muller, D. C.; Nothofer, H. G.; Scherf, U.; Neher, D.; Brauchle, C.; Meerholz, K. *Nature* (*London*) **2000**, *405*, 661. (c) Muller, D. C.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wlederhirm, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerhotz, K. *Nature* (*London*) **2003**, *421*, 829. (d) Hou, Q.; Zhang, Y.; Li, F. Y.; Peng, J. B.; Cao, Y. *Organometallics* **2005**, *24*, 4509.

(2) Li, B. S.; Li, J.; Fu, Y. Q.; Bo, Z. S. *J. Am. Chem. Soc.* **2004**, *126*, 3430.

(3) (a) Chen, C. T. *Chem. Mater.* **2004**, *16*, 4389. (b) Tang, C. W.; VanSiyke, S. A.; Chen, C H. *Appl. Phys. Lett.* **1989**, *65*, 3610. (c) Picciolo, L. C.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **2001**, *78*, 2378.

(4) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* (*London*) **1998**, *395*, 151. (b) Kwong, R. C.; Sibley, S.; Dubovoy, T.; Baldo, M.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 3709. (c) Guo, T. F.; Chang, S. C.; Yang, Y.; Kwong, R. C.; Thompson, W. E. *Org. Electrochem.* **2000**, *1*, 15.

(5) Tang, C. W.; Van Slyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(6) (a) Bulovic, V.; Shoustikov, A.; Baldo, M. A.; Bose, E.; Kozlov, V. G.; Thompson, M. E.; Forrest, S. R. *Chem. Phys. Lett.* **1998**, *287*, 455. (b) Hamada, Y.; Kanno, H.; Tsujioka, T.; Takahashi, H.; Usuki, T. *Appl. Phys. Lett.* **1999**, *75*, 1682. (c) Tao, X. T.; Miyata, S.; Sasabe, H.; Zhang, G. J.; Wada, T.; Jiang, M. H. *Appl. Phys. Lett.* **2001**, *78*, 279. (d) Picciolo, L. C.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **2001**, *78*, 2378.

(7) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58.

(8) (a) Iabal, R.; Yahioglu, G.; Milgrom, L.; Moratti, S. C.; Holmes, A. B.; Cacialli, F.; Morgado, J.; Friend, R. H. *Synth. Met.* **1999**, *102*, 1024. (b) Iqbal, R.; Moratti, S. C.; Holmes, A. B.; Yahioglu, G.; Milgrom, L. R.; Cacialli, F.; Morgado, J.; Friend, R. H. *J. Mater. Sci.: Mater. Electron.* **2000**, *11*, 97. (c) Morgado, J.; Cacialli, F.; Friend, R. H.; Iqbal, R.; Yahioglu, G.; Milgrom, L. R.; Moratti, S. C.; Holmes, A. B. *Chem. Phys. Lett.* **2000**, *325*, 552. (d) Morgado, J.; Cacialli, F.; Iqbal, R.; Moratti, S. C.; Holmes, A. B.; Yahioglu, G.; Milgromd, L. R.; Friend, R. H. *J. Mater. Chem.* **2001**, *11*, 278. (e) Lo, S. C.; Burn, P. L. *Synth. Met.* **1999**, *102*, 1089. (f) Fei, Z. P.; Li, B. S.; Bo, Z. S.; Lu, R. *Org. Lett.* **2004**, *6*, 4703.

(9) Li, B. S.; Xu, X. J.; Sun, M. H.; Fu, Y. Q.; Yu, G.; Liu, Y. Q.; Bo, Z. S. *Macromolecules* **2006**, *39*, 456.

(10) Liu, X. M.; He, C. B.; Hao, X. T.; Tan, L. W.; Li, Y. Q.; Ong, K. S. *Macromolecules* **2004**, *37*, 5965.

(11) (a) Kannan, R.; He, G. S.; Lin, T. C.; Prasad, P. N. *Chem. Mater.* **2004**, *16*, 185. (b) Ding, J. F.; Day, M.; Robertson, G.; Roovers, J. *Macromolecules* **2002**, *35*, 3474.

(12) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

(13) Xin, Y.; Wen, G. A.; Zeng, W. J.; Zhao, L.; Zhu, X. R.; Fan, Q. L.; Feng, J. C.; Wang, L. H.; Wei, W.; Peng, B.; Cao, Y.; Huang, W. *Macromolecules* **2005**, *38*, 6755.

(14) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(15) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(16) (a) Morgado, J.; Cacialli, F.; Friend, R. H.; Iqbal, R.; Yahioglu, G.; Milgrom, L. R.; Moratti, S. C.; Holmes, A. B. *Chem. Phys. Lett.* **2000**, *325*, 552. (b) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610. (c) Hsieh, B. Y.; Chen, Y. *Macromolecules* **2007**, *40*, 8913.

(17) (a) Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243. (b) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.

(18) Prommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(19) (a) Yang, J.; Jiang, C. Y.; Zhang, Y.; Yang, R.; Yang, W.; Hou, Q.; Cao, Y. *Macromolecules* **2004**, *37*, 1211. (b) Xia, C. J.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854.

(20) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

(21) Redecker, M.; Bradley, D. D. C.; Inbasekaran, M. E.; Woo, P. *Appl. Phys. Lett.* **1998**, *73*, 1565.

(22) (a) Sun, Q. J.; Fan, B. H.; Tan, Z. A.; Yang, C. H.; Li, Y. F.; Yang, Y. *Appl. Phys. Lett.* **2006**, *88*, No. 163510. (b) Sun, Q. J.; Hou, J. H.; Yang, C. H.; Li, Y. F.; Yang, Y. *Appl. Phys. Lett.* **2006**, *89*, No. 153510. (c) Zhou, Y.; Sun, Q. J.; Tan, Z. A.; Zhong, H. Z.; Yang, C. H.; Li, Y. F. *J. Phys. Chem. C* **2007**, *111*, 6862. (d) Zhou, Y.; He, Q. G.; Yang, Y.; Zhong, H. Z.; He, C.; Yang, C. H.; Liu, W.; Bai, F. L.; Li, Y. F. *Adv. Funct. Mater.* **2008**, *18*, 3299.

(23) (a) Montes, V. A.; Perez-Bolivar, C.; Agarwal, N.; Shinar, J.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2006**, *128*, 12436. (b) Zhang, X. H.; Xie, Z. Y.; Wu, F. P.; Zhou, L. L.; Wong, O. Y.; Lee, C. S.; Kwong, H. L.; Lee, S. T.; Wu, S. K. *Chem. Phys. Lett.* **2003**, *382*, 561.

(24) Yang, Y.; Zhou, Y.; He, Q. G.; He, C.; Yang, C. H.; Bai, F. L.; Li, Y. F. *J. Phys. Chem. B* **2009**, *113*, 7745.