Poly(aryl ether)s Containing Ter- and Pentafluorene Pendants for Efficient Blue Light Emission

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Received October 22, 2005; Revised Manuscript Received December 9, 2005

ABSTRACT: Four novel thermally stable poly(aryl ether)s, e.g., **P3F**, **P5F**, **P2A3F**, and **P2A5F**, containing ter- or pentafluorene units in the side chains for efficient blue light emission have been designed and synthesized. All the polymers show the optical properties identical to the corresponding monomers and are amorphous with higher glass transition temperature (T_g) than their monomeric counterparts. The polymer light-emitting diodes (PLEDs) were fabricated with the device structure of ITO/(PEDOT:PSS)/polymer/Ca/Al. The incorporation of diphenylamine group to oligofluorene terminals significantly reduces the hole-injection energy barrier in PLEDs. The devices based on **P2A3F** and **P2A5F** show the luminous efficiencies of 1.2 and 2.0 cd/A at a brightness of 300 cd/m^2 with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.15, 0.13) and (0.19, 0.20), respectively. All these indicate that the high-performance light-emitting polymers can be synthesized with the traditional condensation polymerization through careful design of polymer structures.

Introduction

Polymer light-emitting diodes (PLEDs) have attracted intensive interest from both industry and scientific society due to their applications in high-quality flat-panel displays.[1] Light-emitting polymers (LEPs) with high photoluminescence (PL) efficiency, great stability, and good processability are critical for fabrication of high-performance PLEDs. Most of LEPs so far are fully conjugated polymers and characterized by complicated morphology due to distribution of molecular weight and presence of chain aggregation and chain entanglement.[2] Moreover, their purification is more difficult in comparison to organic small molecules and oligomers due to lack of appropriate method. Especially for LEPs synthesized by means of cross-coupling reaction catalyzed by transition metal catalyst, for instance for polyfluorenes (PFs), removing residual catalysts is still a great challenge.[3]

In contrast to polymeric counterparts, monodisperse conjugated oligomers are characterized by structural uniformity and regularity, chemical purity and solubility, and well-defined optical properties.[4] Incorporating oligomeric units with well-defined structure into a polymeric skeleton through traditional polymerization (i.e., radical polymerization and condensation polymerization) should be able to take advantages of both polymeric and oligomeric materials. In this circumstance, the optical properties of the polymers are mainly determined by the oligomeric units, and their thermal properties and morphology in the solid state should be able to be modulated through designing appropriate polymer structure. Indeed, several series of condensation LEPs (such as polyesters, polyethers, polyamides, and polyurethanes) have been reported with the conjugated oligomeric units as building blocks of polymer main chain.[1b,c,5,6] For instances, Chen and Leclerc have reported polyethers and polyesters with oligo(phenylenevinylene) units and fluorene/thiophene cooligomer units in polymer chain, respectively.[6] Some polyolefins carrying photoluminescent units have also been reported.[7] However, most of these polymers exhibited electroluminescent properties inferior to those of fully conjugated polymers due to low photoluminescence efficiency,[5e,6d] significant charge carrier trapping,[6b] difficult charge injection, or poor charge carrier transport ability.[5g]

In this paper, we designed and synthesized a series of novel efficient blue light-emitting poly(aryl ether)s (PAEs) containing oligofluorene units as pendant groups, and their optical and thermal properties as well as electroluminescent properties were characterized. Oligofluorenes with different number of fluorene units were chosen owing to their high photoluminescence quantum yield, great thermal stability, and ease of modulation of optical properties.[4,8] Poly(aryl ether) was selected as the polymer skeleton due to its high glass transition temperature, high thermal stability, and excellent film formation capability.[9]

Results and Discussion

Design Concept, Synthesis, and Characterization of Polymers. Structures and cartoon of light-emitting PAEs in the current paper are depicted in Chart 1. Polymers **P3F/P2A3F** and **P5F/P2A5F** carry oligofluorene segments with three and five fluorene units, respectively. Diphenylamine end-cappers, which are favorable for improving hole injection in PLED devices as reminded by recent publications on PFs and oligofluorenes,[10] were introduced into the polymers **P2A3F** and **P2A5F**. All oligofluorene segments in the four polymers are connected with PAE main chain through two phenyl rings at the 9-position of the central fluorene unit. Owing to the sp^3 characteristic of the bridge carbon (9-position) of fluorene, all oligofluorene segments locate nearly perpendicular to the PAE main chain. This three-dimensional structure is favorable of stable glass formation and high glass transition temperature (T_g) of the polymers. Moreover, the optical properties of the polymers should be only dependent on the properties of oligofluorene segments, and the polymer main chain mainly serves as a supporter and a skeleton to control the condensed state of the

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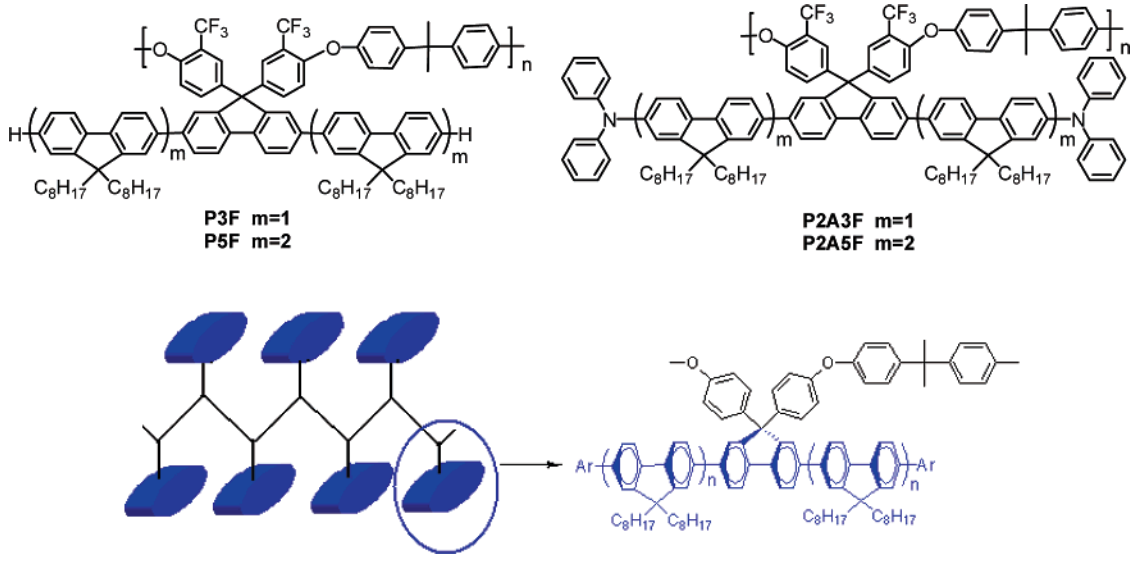
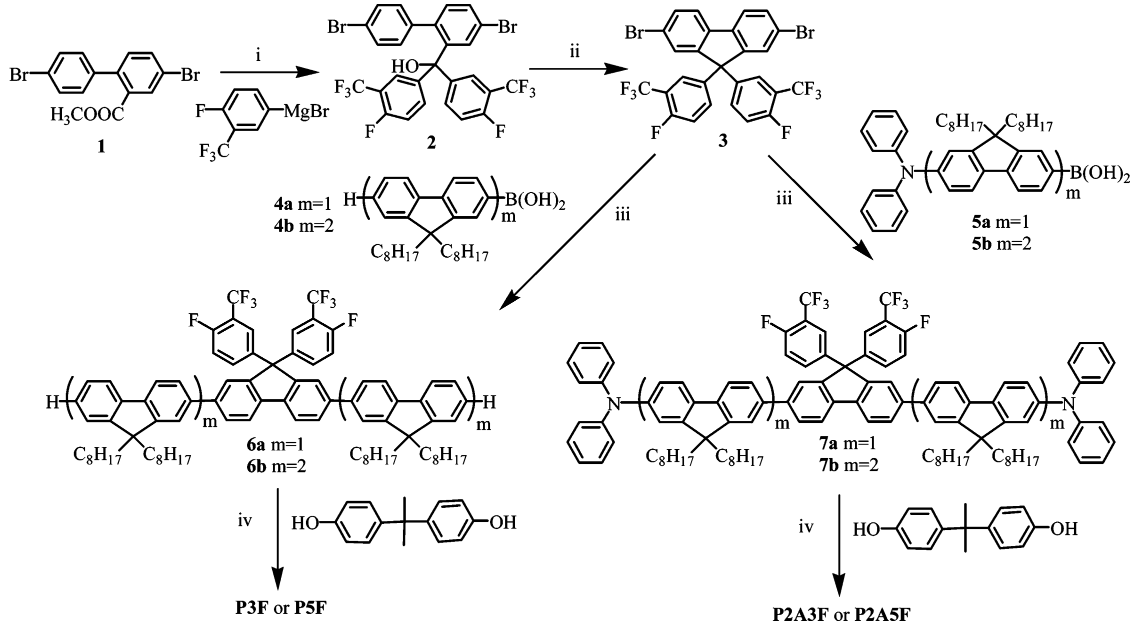
10.1021/ma052282z CCC: \$33.50

Chart 1. Structures and Design Concept of the Poly(aryl ether)s



Scheme 1. Synthesis of Poly(aryl ether)s[a]



[a] (i) Ethyl ether, reflux; (ii) AcOH, H_2SO_4, reflux; (iii) $Pd(PPh_3)_4$, Na_2CO_3 (2.0 M aq), toluene; (iv) K_2CO_3, toluene, DMSO, 140 then 170 °C.

polymers. Please also note that in these polymers there are not any functional groups, such as ester and amide, that are possible photoluminescence quenchers, and the effect of insulating PAE main chain on charge transporting properties of the polymers should be very small due to its relatively small weight ratio, which is 36%, 23%, 29%, and 20% in **P3F**, **P2A3F**, **P5F**, and **P2A5F**, respectively.

The synthesis of monomers and polymers are shown in Scheme 1. Compound **3** was synthesized in two steps with a total yield of 33%. The oligofluorene monomers **6** and **7** were synthesized by means of typical Suzuki coupling in a yield of 70−80%. All four polymers were synthesized from the nucleophilic displacement reaction of 4,4′-dihydroxydiphenylpropane with bis(fluoride)monomers **6** and **7**, a typical condensation polymerization for synthesis of PAEs. Since the polymers precipitated from the solvent DMSO during polymerization, the molecular weight of the polymers is relatively low. The weight-average molecular weight (M_w) and polydispersion index (PDI) of the polymers, determined by gel permeation chromatography (GPC) using polystyrene as the standard, are (1.2−3.46) × 10^4 g/mol and 1.31−1.49, respectively, as shown in Table 1, indicating polymerization degree of around 10. We expect to increase molecular weight by choosing appropriate solvent to increase the solubility of the polymers. All the polymers are soluble in common organic solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran. The structures of all polymers were verified with ^{1}H NMR spectra and the elemental analysis.

Thermal Properties. Thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a scan rate of 10 °C/min under a nitrogen atmosphere, and the results are listed in Table 1. The DSC of **6** and **7** were also characterized for comparison. As revealed in Figure 1a and Table 1, all polymers exhibit decomposition temperature above 389 °C. Figure 1b shows the DSC scans of **P3F**, **P5F**, **P2A3F**, and **P2A5F**. The polymers **P3F**, **P5F**, **P2A3F**, and **P2A5F** exhibit a clear glass transition at 108, 83, 124, and 97 °C, respectively, without any other transition corresponding to recrystallization or crystal melting. Moreover, no anisotropic phase was observed at the

Table 1. Weight-Average Molecular Weight (M_w), Polydispersity Index (PDI), Glass Transition Temperature (T_g), Decomposition Temperature (T_d), and Absorption and Photoluminescence Maxima ($\lambda_{abs,max}$ and $\lambda_{PL,max}$) of the Polymers

						$\lambda_{abs,max}$ (nm)[d]		$\lambda_{PL,max}$ (nm)[d]	
polymer	M_w ($\times 10^4$)[a]	PDI[a]	T_g (°C)	T_d (°C)[b]	Φ_{FL}[c] (%)	solution	film	solution	film
P3F	1.92	1.45	108	415	98	349	349	397, 417	403, 423
P5F	2.71	1.33	83	390	100	370	375	414, 435	420, 440
P2A3F	1.20	1.31	124	411	86	391	392	437	452
P2A5F	3.46	1.49	97	389	85	387	388	430	441

[a] M_w and PDI values of the polymers were determined with GPC in THF using polystyrene as the standard. [b] Onset decomposition temperature measured by TGA under nitrogen. [c] Fluorescence quantum efficiency was measured in toluene with a chromophore concentration of 10^{-7} M and 9,10-diphenylanthracene ($\Phi = 0.9$) as the standard. [d] Solution spectra were measured in toluene with a concentration of 10^{-5} M (terfluorene or pentafluorene units); The films were spin-cast from CH_3Cl solution with the concentration of 8 mg/mL. The excitation wavelength for PL measurements is 340 nm.

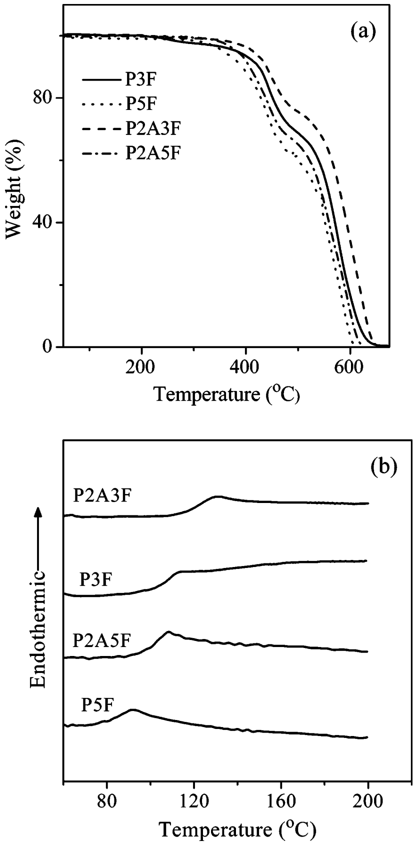


Figure 1. TGA (a) and DSC (b) curves of the polymers **P3F**, **P5F**, **P2A3F**, and **P2A5F**.

Table 2. Glass Transition Temperature (T_g), Absorption, and Photoluminescence Maxima ($\lambda_{abs,max}$ and $\lambda_{PL,max}$) of Compounds 6 and 7

compd	T_g (°C)	$\lambda_{abs,max}$ (nm)[a]	$\lambda_{PL,max}$ (nm)[a]	Φ_{FL}[b] (%)
6a		349	396, 417	97
6b	39	370	413, 435	95
7a	76	391	437	85
7b	71	387	430	81

[a] Solution spectra were measured in toluene with a concentration of 10^{-5} M. [b] Fluorescence quantum efficiency was measured in toluene with a concentration of 10^{-7} M and 9,10-diphenylanthracene ($\Phi = 0.9$) as the standard.

temperature above T_g under a polarizing optical microscope. These indicate that all these polymers are glassy materials, which is believed to be a favorable characteristic of morphological stable LEPs. It is interesting that all polymers show much higher T_g than the corresponding monomers, as shown in Tables 1 and 2. As an example, **P2A3F** shows a T_g of 124 °C, 48 °C higher than that of the monomer **7a**. We propose that the rigid PAE can significantly restrict the movement of the oligofluorene segments and increase the T_g. The diphenylamine end-capping also results in a T_g elevation of 14−16 °C with comparing the T_g of **P2A3F** and **P2A5F** with that of **P3F** and **P5F**. It is worthy to note that all four polymers exhibit higher T_g than a most studied fluorene homopolymer, poly(9,9-dicotylfluorene) (PFO, with a T_g of 75 °C).[11] Therefore, one can expect better morphological stability of current polymers.

Optical Properties. Both absorption and PL spectra of the monomers **6a**, **6b**, **7a**, and **7b** as well as the four polymers are measured in toluene with the concentration of the oligofluorene segments at 10^{-5} M. As shown in Figure 2, Table 1, and Table 2, the solution absorption and PL spectra of the polymers are almost the same with those of the monomers **6** and **7**. With 9,10-diphenylanthracene as the standard, the PL quantum yields (Φ_{PL}) of the polymers are 98%, 86%, 100%, and 85% for **P3F**, **P2A3F**, **P5F**, and **P2A5F**, respectively, also identical to that of the monomers **6** and **7**. These suggest that the optical properties of polymers are only determined by the monomers **6** and **7**. The introduction of the diphenylamine terminals results in ~10% reduction of the PL quantum yield. However, the Φ_{PL} of the polymers **P2A3F** and **P2A5F** (Table 1) is still above 80%, comparable with that of the standard. The absorption and PL spectra of the polymers containing diphenylamine end-capped oligofluorene segments, namely **P2A3F** and **P2A5F**, show a distinct red shift relative to those of **P3F** and **P5F** because of the strong electron donation effect of the diphenylamine groups, which elevates the HOMO level almost without disturbing the LUMO level of the polymers (as shown in the next section). The films of the polymers were spin-cast from chloroform solution with a concentration of 8 mg/mL and spin rate of 1500 rpm. While the film absorption spectra only show a red shift less than 5 nm in comparison to solution ones, the film PL spectra exhibit an apparent red shift up to 15 nm relative to those in solution. In the film state, because of the self-absorption effects, the intensity of the emission peak at the shorter wavelength is relatively lower than that at the longer wavelength, in contrast to the emission spectra in solution. This phenomenon was also observed in PFs.[13] The polymer **P2A3F** and monomer **7a** exhibit the absorption and PL emission at the longer wavelength than **P2A5F** and **7b**. This is probably owing to the reduced conjugation between two diphenylamine end-cappers with increasing the number of fluorene unit in each oligofluorene segment from **P2A3F**/**7a** to **P2A5F**/**7b**. Similar to diphenylamine end-capped oligofluorenes[10b], the PL spectra of **P2A3F** and **P2A5F** show less resolved emission bands, probably attributed to the reduced rigidity of excited states due to introduction of diphenylamine groups.

It is well-known that a serious problem of fluorene homopolymers is their spectral stability upon annealing.[4c] To test the spectral stability of current polymers, a film of **P2A5F** was annealed at 180 °C under vacuum for 22 h. As shown in Figure 3b, the PL spectra before and after annealing are very close, indicative of excellent spectral stability. In contrast, a PFO (with

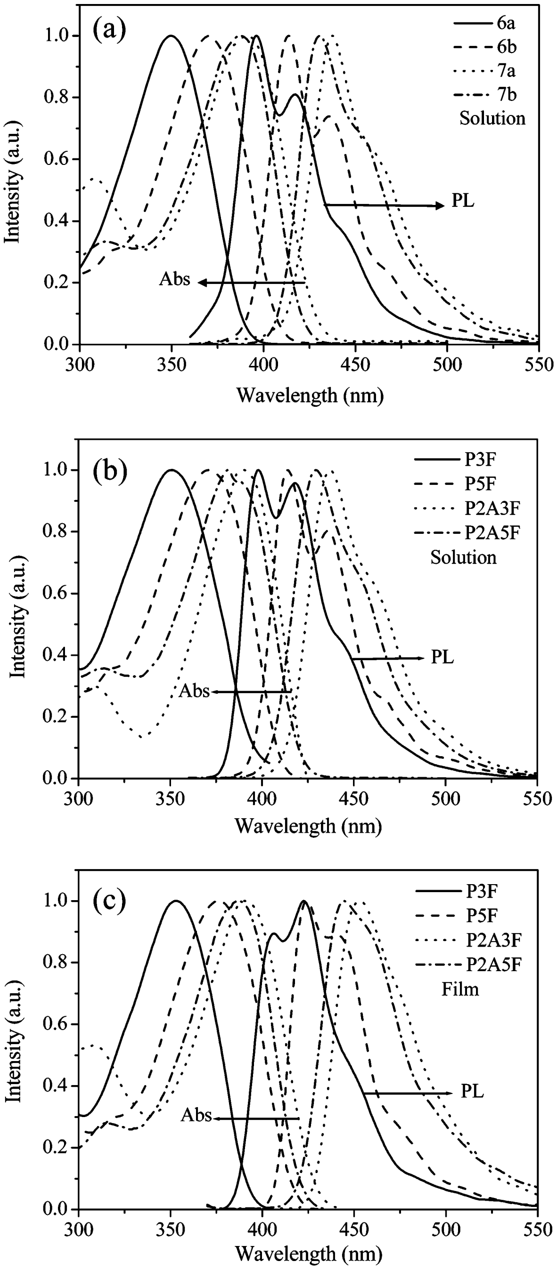


Figure 2. Absorption and PL spectra of monomers (a) and polymers (b) in chloroform solution with an oligofluorene segment concentration of 10^{-5} M and film absorption and PL spectra of the polymers (c).

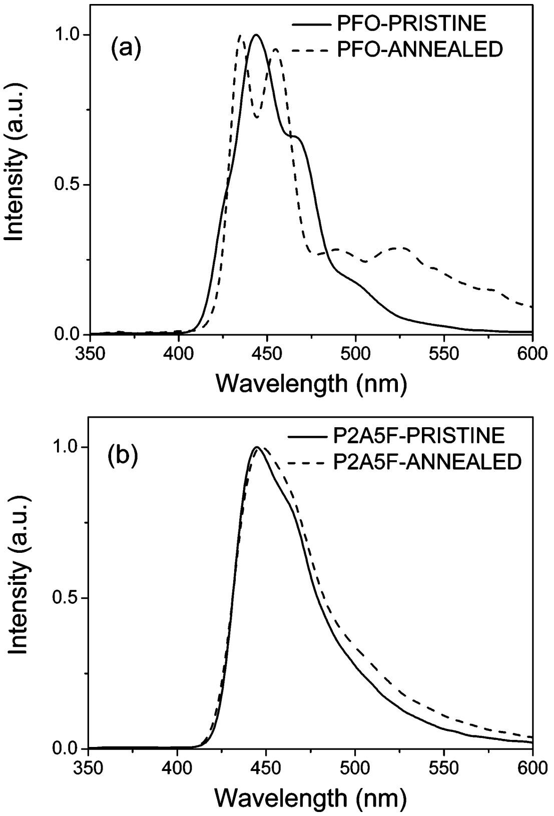


Figure 3. PL spectra of PFO (a) and **P2A5F** (b) films before and after thermal annealing at 180 °C under vacuum for 22 h.

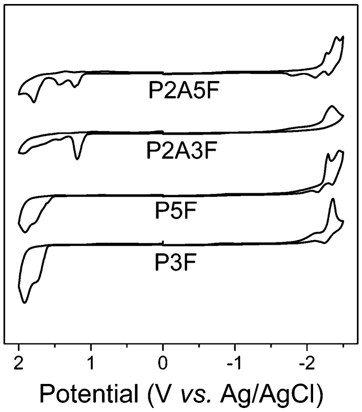


Figure 4. Cyclic voltammograms of the polymers vs Ag/AgCl.

the number-average weight of 110 000 g/mol and PDI of 4.5) film shows a new emission peak at around 520 nm after the same treatment (Figure 3a). This indicates that our PAE type polymers have better spectral stability against thermal annealing than PFO. This is consistent with the amorphous characteristics of our polymers. In particular, the rigid macromolecular structure along with the molecular geometry depicted in Chart 1 limits the close packing of the oligofluorene segments.

Electrochemical Properties. The electrochemical properties of the polymers were investigated by means of cyclic voltammetry with a typical three-electrode cell. Figure 4 shows the cyclic voltammetry curves of the polymers, and Figure 5a shows the energy level diagram. From the onset potential of the oxidation and reduction, the HOMO and LUMO energy levels of the polymers can be estimated. The polymers **P3F** and **P5F** show the HOMO level of 5.9 and 5.8 eV along with LUMO level of 2.1 and 2.2 eV, respectively. Introduction of diphenylamine end-cappers causes an elevation of HOMO level to 5.4 eV for **P2A3F** and **P2A5F**, while the LUMO level is kept the same with that of **P3F** and **P5F**. In other words, the HOMO and LUMO levels of diphenylamine end-capped polymers **P2A3F** and **P2A5F** are determined by diphenylamine end-cappers and conjugated oligofluorene segment, respectively.

Device Properties. The PLEDs were fabricated with a configuration of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS, 50 nm)/polymer (102−129 nm)/Ca/Al, and the device performances are summarized in Table 3. The polymers exhibit electroluminescence (EL) spectra identical to their PL counterparts (Figure 5b). The current density−driving voltage−brightness curves and luminous efficiency−current density relationship are shown in Figure 6 and Figure 7, respectively. Among the four polymers, **P3F** exhibits the worst EL properties, and its maximum brightness can only reach 10 cd/m^2. With five fluorene units in each oligofluorene segment, **P5F** shows significantly improved EL performance. A luminous efficiency of 0.6 cd/A at 300 cd/m^2 and a maximum

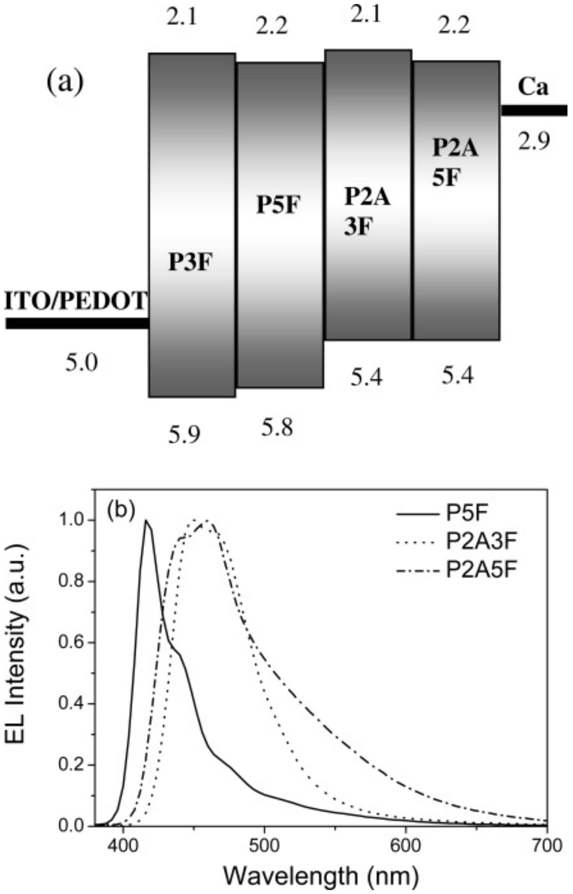


Figure 5. Energy diagram (a) and the EL spectra (b) of the polymers.

brightness of 691 cd/m^2 were realized. These values are comparable to those of the device based on PFO in the same condition. In comparison with **P3F** and **P5F**, the polymers **P2A3F** and **P2A5F** show much better EL performance due to diminished hole-injection energy barrier. Luminous efficiencies of 1.2 and 2.0 cd/A at a brightness of 300 cd/m^2 along with the maximum brightness of 1751 and 4605 cd/m^2 for **P2A3F** and **P2A5F**, respectively, are realized. This improvement of EL performance is consistent with Scherf's observations in triarylamine end-capped PFs.[10a] In fact, the turn-on voltage is 3.5 V for the devices of both **P2A3F** and **P2A5F**, much lower than 10.0 and 6.5 V for the devices based on **P3F** and **P5F**. It is worthy to point out that the luminous efficiencies of the current polymers only slightly decrease with increasing brightness. For example, the luminous efficiencies of the devices based on **P2A3F** and **P2A5F** at a brightness of 1000 cd/m^2 are still as high as 1.1 and 1.8 cd/A, respectively, with only ~10% reduction in comparison to those at the brightness of 300 cd/m^2. The Commission Internationale de L'Eclairage (CIE) coordinates are (0.17, 0.09), (0.15, 0.13), and (0.19, 0.20) for **P5F**, **P2A3F**, and **P2A5F**, respectively, and are almost independent of driving voltage.

Conclusions

We have designed and synthesized a series of novel light-emitting PAEs with oligofluorene segments connected in the side chains. The PAE main chain in combination with a rigid and insulating linkage between polymer main chain and oligofluorene segments endows the light-emitting PAEs glass-forming ability and high T_g, therefore good morphological stability. The optical properties mainly depend on the structures of oligofluorene segments. Because of the small weight ratio of main chain in the polymers, the insulating PAE skeleton has a negligible effect on the polymer optoelectronic properties. With five fluorene units in each oligofluorene segment, the polymer **P5F** shows the identical EL performance with fluorene homopolymer. The introduction of diphenylamine end-cappers can feasibly modulate the HOMO level of the polymers to reduce the hole-injection energy barrier in PLED devices and hence improve the device performance. The ease of synthesis and purification, the defined optical properties, and the high EL performance of current light-emitting PAEs indicate that the traditional condensation polymerization is a promising alternative approach to synthesizing high-performance LEPs with the appropriate structural design.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO) was vacuum-distilled from finely powdered calcium hydride. Tetrahydrofuran (THF) and toluene were distilled over sodium/ benzophenone. The compound 5-bromo-2-fluorobenzotrifluoride was purchased from Apollo scientific Ltd. All other chemicals, reagents, and solvents were used as received from commercial sources without further purification.

2,7-Dibromo-9,9-bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorene (3). The compound 5-bromo-2-fluorobenzotrifluoride (0.972 g, 4.00 mmol) in anhydrous diethyl ether (30 mL) was slowly added to a flask containing clean magnesium flakes (0.194 g, 8.00 mmol). The mixture was refluxed for 3 h under a nitrogen atmosphere, and then compound **1**[12] (0.50 g, 1.3 mmol) was slowly added with a solid dropping funnel. The resulting mixture was refluxed for 3 h followed by the addition of saturated NH_4Cl aqueous solution and extracted with diethyl ether. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. After the solvent had been removed, the residue containing crude compound **2** was dissolved in (50 mL) acetic acid with 2 mL of concentrated sulfuric acid, and the mixture was refluxed for 3 h. After the mixture was cooled to room temperature, a large amount of dichloromethane was added. The organic phase was washed with water and dried over anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane 5/1) to afford the compound **3** as a white solid with a yield of 33%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H, $J = 8.1$ Hz), 7.61 (dd, 2H, $J = 8.1$ Hz, 1.5 Hz), 7.41 (d, 2H, $J = 1.5$ Hz), 7.39−7.32 (m, 4H), 7.19 (t, 2H, $J = 9.0$ Hz).

General Procedure for Preparation of Compounds 6 and 7 via Suzuki Coupling Reaction. Toluene and a 2.0 M aqueous solution of K_2CO_3 (15 equiv; toluene/water at a 3:2 volume ratio) were added to a two-necked round-bottom flask containing compound **3** (1 equiv), compound **4**[4c] or **5**[10b] (2.2 equiv), and Pd(PPh_3)$_4$ (3 mol %). The reaction mixture was stirred thoroughly at 80 °C for 2 days followed by the addition of a large amount of dichloromethane. The organic portion was washed with brine and dried over anhydrous $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel to afford the target compound with a yield of 70−80%.

6a. Yield: 71%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, 2H, $J = 7.8$ Hz), 7.77−7.75 (m, 4H), 7.72 (d, 2H, $J = 7.2$ Hz), 7.57−7.55 (m, 4H), 7.51−7.48 (m, 6H), 7.36−7.31 (m, 6H), 7.15 (t, 2H, $J = 9.0$ Hz), 1.99−1.96 (m, 8H), 1.18−0.66 (m, 60H). MS (Maldi-TOF): *m*/*z*: 1266.7 [M$^+$].

6b. Yield: 78%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, 2H, $J = 7.8$ Hz), 7.80−7.77 (m, 8H), 7.74 (d, 2H, 7.2 Hz), 7.67−7.57 (m, 12H), 7.54 (d, 2H, $J = 7.8$ Hz), 7.52−7.50 (m, 4H), 7.37−7.30 (m, 6H), 7.17 (t, 2H, $J = 9.0$ Hz), 2.06−2.02 (m, 16H), 1.20−0.77 (m,120H). MS (Maldi-TOF): *m*/*z*: 2044.5 [M$^+$].

7a. Yield: 73%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, 2H, $J = 8.4$ Hz), 7.74 (d, 2H, $J = 7.8$ Hz), 7.64 (broad, 2H), 7.58−7.55 (m, 6H), 7.48 (d, 4H, $J = 7.8$ Hz), 7.44 (s, 2H), 7.24 (broad, 8H), 7.16−7.13 (m, 12H), 7.01 (broad, 6H), 1.88−1.84 (m, 8H), 1.22−0.68 (m, 60H). MS (Maldi-TOF): *m*/*z*: 1601.9 [M$^+$].

Table 3. Turn-On Voltage (V_{on}), Maximum Brightness (L_{max}), Luminous Efficiency (LE), Maximum Power Efficiency (PE_{max}), and CIE Coordinates of the Devices with the Configuration of ITO/PEDOT/Polymer/Ca/Al

polymer	$\lambda_{EL,max}$ (nm)	V_{on}[a] (V)	L_{max} (cd/m^2)	LE[b] (cd/A)	LE[c] (cd/A)	PE_{max} (lm/W)	CIE (*x*, *y*)[b]
P3F	401, 420	10.0	10			0.0	
P5F	419, 440	6.5	691	0.6		0.2	0.17, 0.09
P2A3F	450, 467	3.5	1751	1.2	1.1	0.6	0.15, 0.13
P2A5F	442, 459	3.5	4605	2.0	1.8	1.0	0.19, 0.20

[a] The voltage at the brightness of 1 cd/m^2. [b] The values at 300 cd/m^2. [c] Luminous efficiency at 1000 cd/m^2.

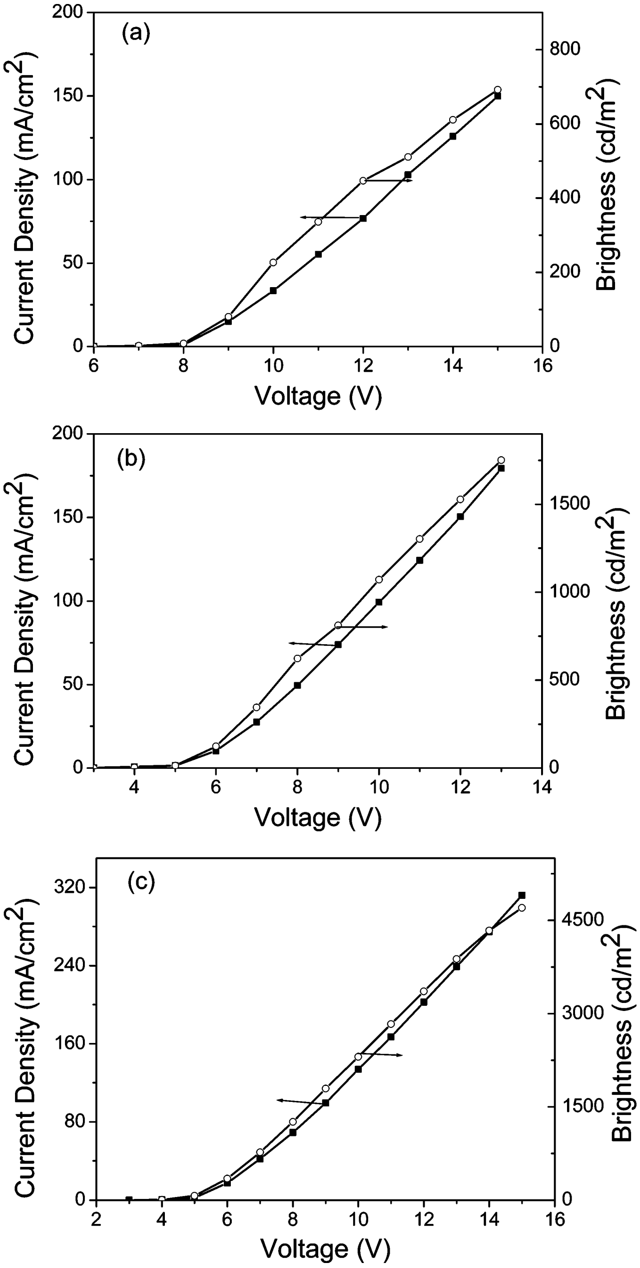


Figure 6. Current density−driving voltage−brightness plots of the devices based on the polymers **P5F** (a), **P2A3F** (b), and **P2A5F** (c).

7b. Yield: 76%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.93 (d, 2H, J = 7.8 Hz), 7.79−7.77 (m, 6H), 7.65−7.58 (m, 16H), 7.53 (d, 2H, J = 8.4 Hz), 7.52−7.50 (m, 4H), 7.25 (broad, 8H), 7.18−7.13 (m, 12H), 7.01 (broad, 6H), 2.17−1.96 (m, 16H), 1.22−0.77 (m, 120H). MS (Maldi-TOF): *m*/*z*: 2378.5 [M$^+$].

General Polymerization Procedure. A mixture of 4,4′-dihydroxydiphenylpropane (0.114 g, 0.50 mmol), bis(fluoride) monomers **6** or **7** (0.52 mmol), toluene (5 mL), DMSO (5 mL), and K$_2$CO$_3$ (0.166 g, 1.2 mmol) in a two-necked 20 mL glass reactor equipped with a Dean−Stark trap was heated to 140 °C for 2.0 h until the toluene was all condensed in the Dean−Stark trap. The reaction temperature was then rose to 170 °C for extra 12 h. Then the mixture was cooled to room temperature and diluted with 200 mL of dichloromethane. The organic portion was washed with water, dried with anhydrous MgSO$_4$, and concentrated into 5 mL. The polymer was precipitated with methanol, followed by purification with Soxhlet extraction with acetone and precipitated into methanol twice. The resulting polymers are white or light-yellow solid with a yield of 50−70%.

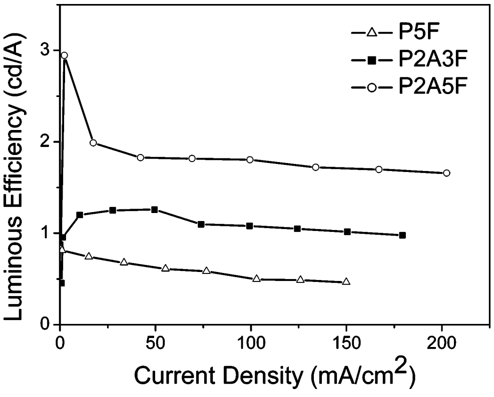


Figure 7. Luminous efficiency−current density relationship of the devices based on the polymers **P5F**, **P2A3F**, and **P2A5F**.

P3F. Yield: 70%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.85 (d, 2H, J = 7.8 Hz), 7.74−7.48 (m, 16H), 7.33−7.30 (m, 6H), 7.16 (d, 4H, J = 8.4 Hz), 6.91 (d, 4H, J = 8.4 Hz), 6.78−6.76 (m, 2H), 2.01−1.96 (m, 8H), 1.59 (s, 6H), 1.22−0.65 (m, 60H). Anal. Calcd for $C_{100}H_{108}F_6O_2$ (%): H, 7.48; C, 82.50. Found: H, 7.25; C, 82.17.

P5F: Yield: 61%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.87 (d, 2H, J = 7.8 Hz), 7.78−7.60 (m, 24H), 7.51−7.50 (m, 4H), 7.35−7.28 (m, 6H), 7.15 (d, 4H, J = 8.4 Hz), 6.91 (d, 4H, J = 8.4 Hz), 6.79−6.77 (m, 2H), 2.04−2.00 (m, 16H), 1.58 (s, 6H), 1.18−0.71 (m, 120H). Anal. Calcd for $C_{158}H_{188}F_6O_2$ (%): H, 8.49; C, 84.98. Found: H, 8.34; C, 84.62.

P2A3F. Yield: 53%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.83 (d, 2H, J = 7.8 Hz), 7.67−7.64 (m, 4H), 7.58−7.55 (m, 6H), 7.47−7.44 (m, 6H), 7.26 (broad, 8H), 7.16−6.89 (m, 24H), 6.79−6.76 (m, 2H), 1.88−1.83 (m, 8H), 1.58 (s, 6H), 1.18−0.68 (m, 60H). Anal. Calcd for $C_{124}H_{130}F_6N_2O_2$ (%): H, 7.30; C, 83.00; N, 1.56. Found: H, 7.02; C, 82.86; N, 1.57.

P2A5F. Yield: 68%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.85 (d, 2H, J = 7.8 Hz), 7.78−7.57 (m, 22H), 7.52−7.51 (m, 6H), 7.25 (broad, 8H), 7.18−6.91 (m, 24H), 6.79−6.76 (m, 2H), 2.04−1.87 (m, 16H), 1.58 (s, 6H), 1.22−0.71 (m, 120H). Anal. Calcd for $C_{182}H_{210}F_6N_2O_2$ (%): H, 8.23; C, 85.00; N, 1.09. Found: H, 8.00; C, 85.02; N, 1.03.

Instrumentation. ^{1}H NMR spectra were recorded with Bruker 300 or 600 MHz FT-NMR spectrometer. All synthesized monomers used for polymerization were confirmed by a LDI-1700 matrix-assisted laser desoption ionization time-of-flight (MALDI TOF) mass spectrometer (American Linear Scientific Inc.). The elemental analysis was performed using a Bio-Rad elemental analysis system. The UV−vis absorption and PL spectra were recorded on a Perkin-Elmer Lambda 35 UV/vis spectrometer and a Perkin-Elmer LS50B luminescence spectrometer, respectively. The cyclic voltammetry was measured on an EG&G model 283 potentiostat/galvanostat system at room temperature using a Ag/AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a platinum plate as the working electrode in acetonitrile solution of (n-Bu)$_4$NClO$_4$ (0.1 M) with a scanning speed of 100 mV/s. Thermal properties of the polymers were measured using Perkin-Elmer DSC7 and TGA7 equipment at a heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Device Fabrication and Characterization. The polymer light-emitting diodes with a configuration of ITO/PEDOT:PSS/polymers/Ca/Al were fabricated by spin-coating polymer solution in chloroform with a concentration of 15 g/mL on the PEDOT:PSS (50 nm) pretreated ITO substrate. The film thickness for polymers **P3F**, **P5F**, **P2A3F**, and **P2A5F** is 102, 129, 120, and 117 nm, respectively. A 10 nm thick calcium layer and a 100 nm thick aluminum layer were deposited by thermal evaporation under a vacuum level of 10^{-3} Torr. The electroluminescence (EL) spectra and current−voltage and brightness−voltage curves of devices were recorded using a Keithley 2400/2000 current/voltage source unit with a calibrated silicon photodiode under ambient conditions.

Acknowledgment. This work was supported by National Natural Science Foundation of China (Project No. 90201022, 20574067 and 50573076) and 973 Project (2002CB613402).

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MA052282Z