

SYNTHESIS AND CHARACTERIZATION OF BLUE LIGHT-EMITTING POLY(ARYL ETHER)S CONTAINING PYRIMIDINE-INCORPORATED OLIGOFLUORENE PENDANTS WITH BIPOLAR FEATURE*

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Abstract Novel blue light-emitting poly(aryl ether)s comprising of bipolar oligofluorene pendants as chromophores have been designed and synthesized, in which pyrimidine and arylamine moieties are utilized as the electron acceptor and electron donor, respectively. Through varying π bridge length from monofluorene to bifluorene and end-cappers from hydrogen to carbazole and diphenylamine, the emission color of the resulting polymers covers from deep blue to greenish blue, and their HOMO and LUMO levels can be modulated to facilitate charge injection to improve the device performance. Polymer light-emitting diodes (PLEDs) are fabricated with the device structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (50 nm)/polymer (80 nm)/Ca (10 nm)/Al (200 nm). Among these polymers, **P2Cz5F-Py** with bifluorene bridge and carbazole end-capper shows excellent trade-off between the efficiency and emission wavelength, having a peak luminous efficiency as high as 1.26 cd/A and Commission Internationale de L'Eclairage (CIE) coordinates of (0.17, 0.17).

Keywords: Poly(aryl ether)s; Pyrimidine; Oligofluorene; Bipolar; PLEDs.

INTRODUCTION

The search of blue light-emitting polymers with excellent electroluminescent (EL) properties has been intensively pursued^[1–3] after the first report of the attractive poly(phenylenevinylene)s-based polymer light-emitting diodes (PLEDs) fabricated by solution process^[4], because full color displays can be realized through down energy transfer by doping green or red dyes into blue matrix^[5–9]. Up to date, the majority of blue polymers are polyfluorenes (PFs) or their derivatives with fully-conjugated backbones^[10, 11]. Unfortunately, they usually suffer from unstable EL spectra^[12, 13] and transition metal catalyst residue^[14]. In contrast, small molecular materials with blue emissions have great advantages of high purity, the ease of structural modification and variation. Among them anthracene-based materials^[15–17] and distyrylarylene (DSA) analogues^[18, 19] have already reached the level of commercialization through the efforts of Kodak and Idemitsu Kosan corporations. Unlike PLEDs, here the use of multilayer device architecture and vacuum deposition technology significantly results in high cost in the device fabrication. Therefore, non-conjugated blue polymers, with spacially isolated small molecular chromophores as a side chain or part of the polymer main chain, may be a compromise between small

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molecules and conjugated polymers, for this platform can provide an enough workaround for small molecules to utilize the solution process while avoiding the catalyst pollution in conjugated polymers. Compared with the fully-conjugated counterparts, however, few non-conjugated polymers following this strategy have been reported owing to their generally poor device performance^[20–22].

Our group has recently prepared a class of blue poly(aryl ether)s (PAEs) containing oligofluorenes in the main chain or side chain *via* alkali-catalyzed aromatic nucleophilic substitution polymerization, and realized comparable EL efficiency with that of the classic poly(octylfluorene)s (PFO)^[23–26]. Despite the effectiveness, the turn-on voltage is somewhat high, which is understandable when considering that the bandgap broadening of organic semiconductors would inevitably result in additional difficulties of charge injection from electrodes. To address this problem, efficient bipolar oligomers with blue emissions need to be further developed. In this case, the electron-donating and -accepting moieties are simultaneously incorporated into a single blue-emitting molecule to facilitate its hole and electron injection/transport capability *via* tuning the highest occupied and/or lowest unoccupied molecular orbital (HOMO/LUMO) levels.

With this idea in mind, in this paper, we designed and synthesized a series of bipolar blue oligomers with pyrimidine as the electron acceptor (A) and aryl amine as the electron donor (D). Then these developed oligomers were covalently connected at the side chain of PAEs to afford novel PAE-based blue light-emitting polymers, and their thermal, optical, electrochemical and EL properties were characterized in detail.

EXPERIMENTAL

Materials

Dimethyl acetamide (DMAc) was vacuum-distilled from finely powdered calcium hydride. Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone. The compound 5-bromo-2-iodopyrimidine was synthesized according to the literatures^[27]. All boronic acid compounds were prepared from bromo-substituted aromatics^[23] following the same synthetic procedures reported before^[28–30]. All other chemicals, reagents, and solvents were used as received from commercial sources without further purification.

General Procedure for the Preparation of Compounds 1, 2 and 3 via Suzuki Coupling Reaction

Toluene and a 2.0 mol/L aqueous solution of Na₂CO₃ (2 equiv, toluene/water at a 5:2 volume ratio) were added to a two-necked round-bottom flask containing 5-bromo-2-iodopyrimidine (1 equiv), aryl boronic acid (1 equiv) and Pd(PPh₃)₄ (2% equiv). The reaction mixture was stirred thoroughly at 90 °C for 1 day followed by the addition of a large amount of dichloromethane. The organic portion was washed with brine and dried over anhydrous Na₂SO₄. The concentrated crude product was purified by column chromatography on silica gel to afford the target compound with a high yield of 75%–85%.

1a: yield: 78%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.90 (s, 2H), 8.48 (d, 1H, J = 8.1 Hz), 8.43 (s, 1H), 7.83 (d, 1H, J = 8.1 Hz), 7.81–7.74 (m, 1H), 7.41–7.37 (m, 3H), 2.06–2.01 (m, 4H), 1.50–0.66 (m, 30H).

1b: yield: 76%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.90 (s, 2H), 8.52 (dd, 1H, J = 7.8 Hz, J = 1.5 Hz), 8.45 (d, 1H, J = 1.5 Hz), 7.86 (d, 2H, J = 8.1 Hz), 7.83–7.66 (m, 8H), 7.43–7.32 (m, 3H), 2.17–2.04 (m, 8H), 1.24–0.77 (m, 60 H).

2a: yield: 85%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.91 (s, 2H), 8.55 (d, 1H, J = 8.1 Hz), 8.49 (s, 1H), 8.22 (d, 2H, J = 7.8 Hz), 8.02 (d, 1H, J = 8.4 Hz), 7.92 (d, 1H, J = 8.1 Hz), 7.63–7.60 (m, 2H), 7.52–7.44 (m, 4H), 7.38–7.29 (m, 2H), 2.19–1.93 (m, 4 H), 1.23–0.80 (m, 30H).

2b: yield: 81%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.88 (s, 2H), 8.48 (d, 1H, J = 8.1 Hz), 8.44 (s, 1H), 8.18 (d, 2H, J = 8.1 Hz), 7.95 (d, 1H, J = 8.4 Hz), 7.88–7.84 (m, 3H), 7.73–7.67 (m, 4H), 7.58–7.84 (m, 3H), 7.73–7.67 (m, 4H), 7.58–7.56 (m, 2H), 7.48–7.41 (m, 4H), 7.37–7.28 (m, 2H), 2.14–2.04 (m, 8H), 1.20–0.76 (m, 60H)

3a: yield: 75%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.87 (s, 2H), 8.46 (dd, 1H, J = 7.8 Hz, J = 1.5 Hz), 8.37 (d, 1H, J = 1.5 Hz), 7.73 (d, 1H, J = 8.1 Hz), 7.64 (d, 1H, J = 8.1 Hz), 7.32–7.27 (m, 2H), 7.19–7.16 (m, 6H), 7.09–7.04 (m, 4H), 2.04–1.87 (m, 4H), 1.25–0.7 (m, 30H).

3b: yield: 80%; ¹H-NMR (300 MHz, CDCl₃, δ): 8.89 (s, 2H), 8.49 (d, 1H, J = 8.1 Hz), 8.45 (s, 1H), 7.86 (d,

2H, $J = 8.1$ Hz), 7.67–7.62 (m, 6H), 7.29–7.17 (m, 10H), 2.16–2.05 (m, 8H), 1.20–0.77 (m, 60H).

General Procedure for the Preparation of Compounds 3F-Py, 5F-Py, 2Cz3F-Py, 2Cz5F-Py, 2A3F-Py and 2A5F-Py via Suzuki Coupling Reaction

Toluene and a 2.0 mol/L 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 bisboronic acid (1 equiv), compound **1**, **2** or **3** (2 equiv), and $Pd(PPh_3)_4$ (2% equiv). The reaction mixture was stirred thoroughly at 80 °C for 1 day 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, then recrystallized in acetone with a yield of 35%–53%.

3F-Py: yield: 45%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.02 (s, 4H), 8.54 (d, 2H, $J = 8.1$ Hz), 8.48 (s, 2H), 8.04 (d, 2H, $J = 8.1$ Hz), 7.83 (d, 2H, $J = 8.1$ Hz), 7.79–7.76 (m, 4H), 7.56–7.44 (m, 4H), 7.41–7.17 (m, 10H), 2.06–2.02 (m, 8H), 1.14–0.65 (m, 60H); MS (MALDI-TOF): m/z : 1423.0 [M^+].

5F-Py: yield: 52%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.02 (s, 4H), 8.56 (d, 2H, $J = 8.1$ Hz), 8.50 (s, 2H), 8.08 (d, 2H, $J = 8.4$ Hz), 7.88–7.65 (m, 18H), 7.56 (s, 2H), 7.50–7.18 (m, 12H), 2.14–2.02 (m, 16H), 1.42–0.74 (m, 120H); MS (MALDI-TOF): m/z : 2201.6 [M^+].

2Cz3F-Py: yield: 53%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.96 (s, 4H), 8.55 (d, 2H, $J = 8.1$ Hz), 8.46 (s, 2H), 8.01 (d, 4H, $J = 7.5$ Hz), 7.98 (d, 2H, $J = 7.8$ Hz), 7.91 (d, 2H, $J = 8.1$ Hz), 7.84 (d, 2H, $J = 7.8$ Hz), 7.72 (d, 2H, $J = 8.1$ Hz), 7.51–7.18 (m, 24H), 2.12–1.90 (m, 8H), 1.20–0.60 (m, 60H); MS (MALDI-TOF): m/z : 1752.1 [M^+].

2Cz5F-Py: yield: 46%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.97 (s, 4H), 8.55 (d, 2H, $J = 8.1$ Hz), 8.46 (s, 2H), 8.11 (d, 4H, $J = 7.8$ Hz), 7.90 (d, 2H, $J = 8.1$ Hz), 7.86 (d, 2H, $J = 8.1$ Hz), 7.80–7.78 (m, 6H), 7.72 (d, 2H, $J = 7.8$ Hz), 7.66–7.60 (m, 8H), 7.48–7.17 (m, 24H), 2.17–1.96 (m, 16H), 1.22–0.77 (m, 120H); MS (MALDI-TOF): m/z : 2530.9 [M^+].

2A3F-Py: yield: 38%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.99 (s, 4H), 8.49 (d, $J = 8.1$ Hz, 3H), 8.41 (s, 2H), 8.03 (d, $J = 8.1$ Hz, 2H), 8.41 (s, 2H), 8.03 (d, $J = 8.1$ Hz, 2H), 7.78–7.71 (m, 4H), 7.61 (d, 8.1 Hz, 2H), 7.54 (s, 2H), 7.48–7.41 (m, 4H), 7.28–6.70 (m, 26H), 1.99–1.96 (m, 8H), 1.35–0.68 (m, 60H); MS (MALDI-TOF): m/z : 1755.7 [M^+].

2A5F-Py: yield: 41%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.05 (s, 4H), 8.58 (d, 2H, $J = 8.1$ Hz), 8.54 (s, 2H), 8.08 (d, 2H, $J = 8.1$ Hz), 7.91–7.47 (m, 24H), 7.32–7.03 (m, 26H), 1.88–1.84 (m, 16H), 1.22–0.68 (m, 120H); MS (MALDI-TOF): m/z : 2535.3 [M^+].

General Polymerization Procedure

A mixture of 4,4'-dihydroxydiphenylpropane (0.114 g, 0.50 mmol), bis(fluoride) monomers **3F-Py**, **5F-Py**, **2Cz3F-Py**, **2Cz5F-Py**, **2A3F-Py** or **2A5F-Py** (0.52 mmol), toluene (5 mL), DMAc (5 mL) and K_2CO_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 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 53%–76%.

P3F-Py: yield: 71%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.02 (s, 4H), 8.54 (d, 2H, $J = 8.1$ Hz), 8.50 (s, 2H), 7.97 (d, 2H, $J = 7.8$ Hz), 7.84 (d, 2H, $J = 7.8$ Hz), 7.79–7.71 (m, 4H), 7.58–7.55 (m, 4H), 7.38–7.22 (m, 8H), 7.20 (d, 4H, $J = 8.4$ Hz), 6.94 (d, 4H, $J = 8.4$ Hz), 6.83 (d, 2H, $J = 8.7$ Hz), 2.01–1.96 (m, 8H), 1.65 (s, 6H), 1.22–0.65 (m, 60H); Anal.Calcd for $C_{108}H_{112}F_6N_4O_2$ (%): C: 80.42, H: 7.06, N: 3.47; Found: C: 79.45, H: 6.97, N: 3.55.

P5F-Py: yield: 74%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.09 (s, 4H), 8.58 (d, 2H, $J = 7.8$ Hz), 8.55 (s, 2H), 8.00 (d, 2H, $J = 7.8$ Hz), 7.90–7.56 (m, 24 H), 7.38–7.35 (m, 6H), 7.20 (d, 4H, $J = 8.4$ Hz), 6.95 (d, 4H, $J = 8.4$ Hz), 6.84 (d, 2H, $J = 8.7$ Hz), 2.12–2.05 (m, 16H), 1.65 (s, 6H), 1.18–0.71 (m, 120H); Anal.Calcd for

$C_{166}H_{192}F_6N_4O_2$ (%): C: 81.45, H: 6.73, N: 4.32; Found: C: 80.84, H: 6.49, N: 2.39.

P2Cz3F-Py: yield: 53%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 9.07 (s, 4H), 8.63 (d, 2H, $J = 8.1$ Hz), 8.58 (s, 2H), 8.19 (d, 4H, $J = 7.6$ Hz, 4H), 7.99–7.96 (m, 4H), 7.92 (d, 2H, $J = 8.1$ Hz), 7.73 (d, 2H, $J = 7.5$ Hz), 7.59–7.29 (m, 22H), 7.20 (d, 4H, $J = 8.7$ Hz), 6.95 (d, 4H, $J = 8.7$ Hz), 6.84 (d, 2H, $J = 8.4$ Hz), 2.20–2.00 (m, 8H), 1.58 (s, 6H), 1.20–0.70 (m, 60H); Anal.Calcd for $C_{132}H_{126}F_6N_6O_2$ (%): C: 81.62, H: 6.54, N: 4.33; Found: C: 80.73, H: 6.66, N: 4.19.

P2Cz5F-Py: yield: 70%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.96 (s, 4H), 8.55 (d, 2H, $J = 8.1$ Hz), 8.46 (s, 2H), 8.09 (d, 4H, $J = 7.8$ Hz), 7.90–7.70 (m, 10H), 7.68–7.55 (m, 10H), 7.50–7.17 (m, 22H), 7.10 (d, 4H, $J = 8.7$ Hz), 6.86 (d, 4H, $J = 8.7$ Hz), 6.74 (d, 2H, $J = 8.4$ Hz), 2.15–1.97 (m, 16 H), 1.56 (s, 6H), 1.16–0.66 (m, 120H); Anal.Calcd for $C_{190}H_{206}F_6N_6O_2$ (%): C, 83.91, H, 7.63, N, 3.09; Found: C: 83.16, H: 7.42, N: 3.17.

P2A3F-Py: yield: 68%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.95 (s, 4H), 8.49 (d, 2H, $J = 8.1$ Hz), 8.40 (s, 2H), 7.89 (d, 2H, $J = 8.1$ Hz), 7.78–7.61 (m, 4H), 7.52–7.46 (m, 4H), 7.38 (s, 2H), 7.16–6.90 (m, 28H), 6.80 (d, 4H, $J = 8.7$ Hz), 6.70 (d, 2H, $J = 8.4$ Hz), 1.88–1.83 (m, 8H), 1.58 (s, 6H), 1.18–0.68 (m, 60H); Anal.Calcd for $C_{132}H_{130}F_6N_6O_2$ (%): C: 81.45, H: 6.73, N: 4.32; Found: C: 80.84, H: 6.49, N: 4.25.

P2A5F-Py: yield: 76%; ^1H -NMR (300 MHz, $CDCl_3$, δ): 8.90 (s, 4H), 8.45 (d, 2H, $J = 8.1$ Hz), 8.39 (s, 2H), 7.83 (d, 2H, $J = 8.1$ Hz), 7.80–7.70 (m, 4H), 7.60–7.40 (m, 18H), 7.18–6.92 (m, 30H), 6.82 (d, 4H, $J = 8.7$ Hz), 6.70 (d, 2H, $J = 8.4$ Hz), 2.04–1.87 (m, 16H), 1.53 (s, 6H), 1.22–0.71 (m, 120H); Anal.Calcd for $C_{190}H_{210}F_6N_6O_2$ (%): C: 83.78, H: 7.77, N: 3.09; Found: C: 83.18, H: 7.53, N: 2.98.

Instrumentation

^1H -NMR spectra were recorded with Bruker 300 MHz or 600 MHz FT-NMR spectrometer. All synthesized monomers used for polymerization were confirmed by a LDI-1700 matrix-assisted laser desorption 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 PerkinElmer Lambda 35 UV/Vis spectrometer and a PerkinElmer 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 $(n-Bu)_4NClO_4$ (0.1 mol/L) with the scanning speed of 100 mV/s. Thermal properties of the polymers were measured using PerkinElmer DSC7 and TGA7 equipment at a heating/cooling rate of 10 K/min under a nitrogen atmosphere. The film thickness was measured with a Dektak surface profilometer (Model 6M).

Polymer Light-emitting Diode (PLED) Fabrication and Measurements

Patterned glass substrates coated with indium tin oxide (ITO) (20 Ω per square) were cleaned with acetone, detergent, distilled water, and then in an ultrasonic solvent bath. After baking in a heating chamber at 120 $^{\circ}C$ for 8 h, the ITO-glass substrates were treated with O_2 plasma for 25 min. Subsequently, a 50-nm-thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Batron-P4083, Bayer AG) film was spin-coated on top of the ITO and then baked at 120 $^{\circ}C$ for 40 min. Then, solutions of the polymers in chlorobenzene were filtered through a filter (0.45 μm) and spin-coated on PEDOT:PSS as the emissive layer (EML). The thickness of the EML was about 80 nm. Successively, the substrate was transferred to a vacuum thermal evaporator, and 10 nm Ca and 200 nm Al were deposited subsequently as the cathode through a shadow mask with an array of 14 mm^2 openings. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current-voltage and brightness-voltage curves of devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

RESULTS AND DISCUSSION

Design Concept, Synthesis and Characterization of Polymers

As shown in Chart 1, six polymers containing PAE main chain and emissive bipolar oligofluorene pendants are

designed. All the pendants are composed of the electron-accepting pyrimidine units, π bridge and electron-donating end-cappers. Here the electron-donating ability of the end-cappers is adjusted from hydrogen to carbazole and diphenylamine units. The π bridge length is also varied from monofluorene to bifluorene to control the conjugation degree as well as the intermolecular charge transfer (ICT) process between the electron donor and electron acceptor. Similar to previous work^[23], these bipolar oligofluorene pendants are connected with the PAE main chain through two phenyl rings at the 9-position of the central fluorene unit. Owing to the sp^3 characteristic of the 9-position carbon, all oligofluorene segments locate nearly perpendicular to the PAE main chain, which does a favor to the formation of stable vitrification and excludes mesophase formation and crystallization. Meanwhile, due to the inert feature of the PAE main chain, the optical properties of the polymers are only determined by the pendants, and the polymer main chain mainly serves as a supporter and a skeleton to control their condensed state.

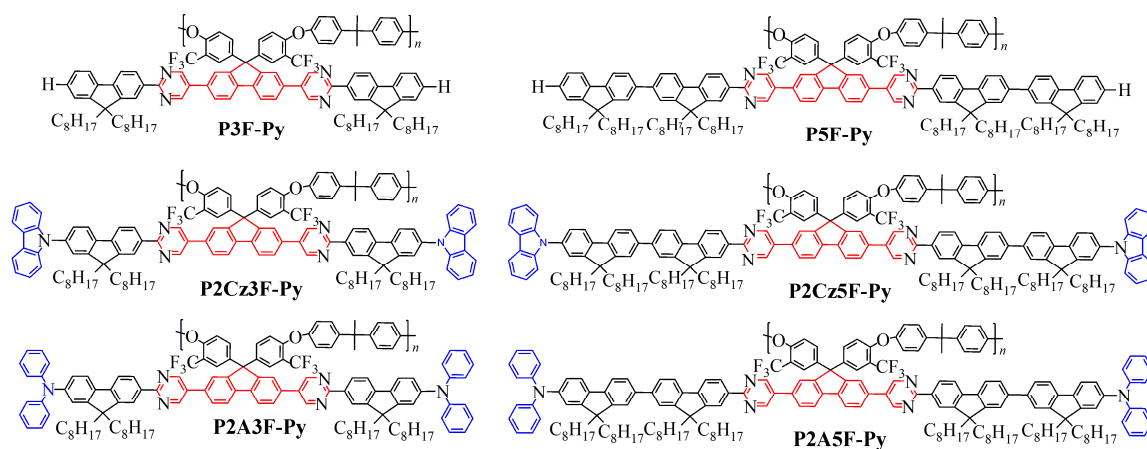
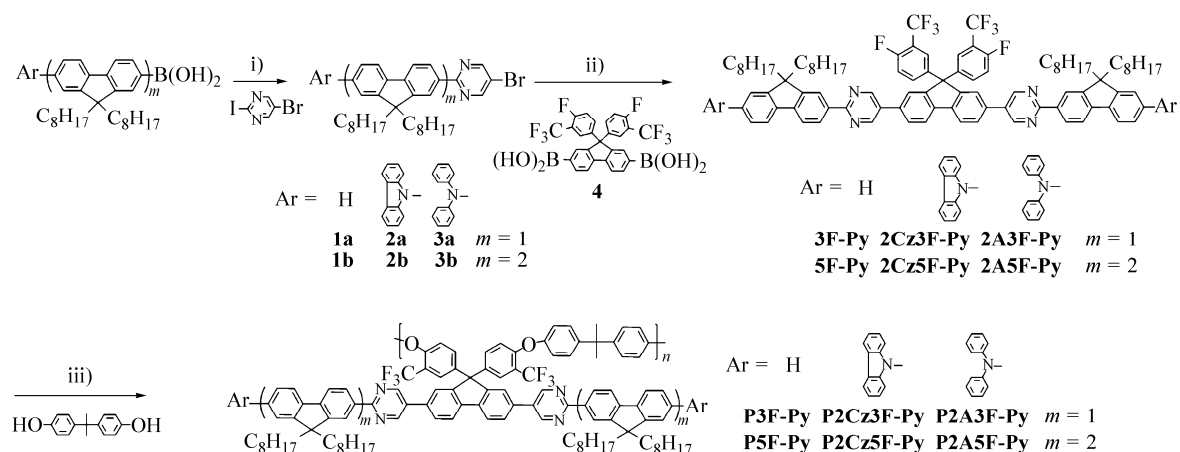


Chart 1 Structures of the poly(aryl ether)s

The synthetic route of monomers and polymers are presented in Scheme 1. Selective Suzuki coupling reaction between oligofluorene boronic acid and 5-bromo-2-iodopyrimidine afforded compounds **1–3** in high yields of 75%–85%, which then reacted with the bisboronic acid intermediate **4** to give the fluorinated monomers. The polymers were prepared by SN_2 nucleophilic polycondensation generally used to produce poly(aryl ether)s^[31]. To reduce the terminal hydroxyl groups in polymers, the feed ratio of fluoro to hydroxyl monomers was controlled at around 1.02. Moreover, dimethylacetamide (DMAc) instead of DMSO was chosen as the polymerization solvent to obtain high molecular weights. As shown in Table 1, the weight-average molecular weights (M_w) of all the polymers, determined by gel permeation chromatography (GPC) using polystyrene as the standard, are at 5.3×10^4 – 28.1×10^4 g/mol, and the polydispersity indexes (PDI) are at the range of 1.41–2.08. The structures of the polymers were verified by ^1H -NMR spectra and elemental analysis (EA). Figure 1 compares the ^1H -NMR spectra of the monomer **2Cz3F-Py** and corresponding polymer **P2Cz3F-Py**. As can be seen from Fig. 1(a), the single peak at $\delta = 8.97$ is assigned to the protons of pyrimidine, while those at $\delta = 7.98$ and 7.72 are assigned to the protons of the centric fluorene. And the circled multiple peaks relate to the protons of the fluorine-substituted phenyl ring. After polymerization, these multiple peaks disappear, and the signals of the protons adjacent to the fluorine atoms become a doublet peak at $\delta = 6.83$, indicative of the leave of fluorine atoms (Fig. 1b). These evidences along with the characteristic signals of the bisphenol A comonomer confirm the occurrence of the nucleophilic polycondensation.



Scheme 1 Synthetic routes of oligofluorene monomers and polymers

i) Pd(PPh₃)₄, 2 mol/L Na₂CO₃, toluene; ii) Pd(PPh₃)₄, 2 mol/L K₂CO₃, THF; iii) K₂CO₃, toluene, DMAc

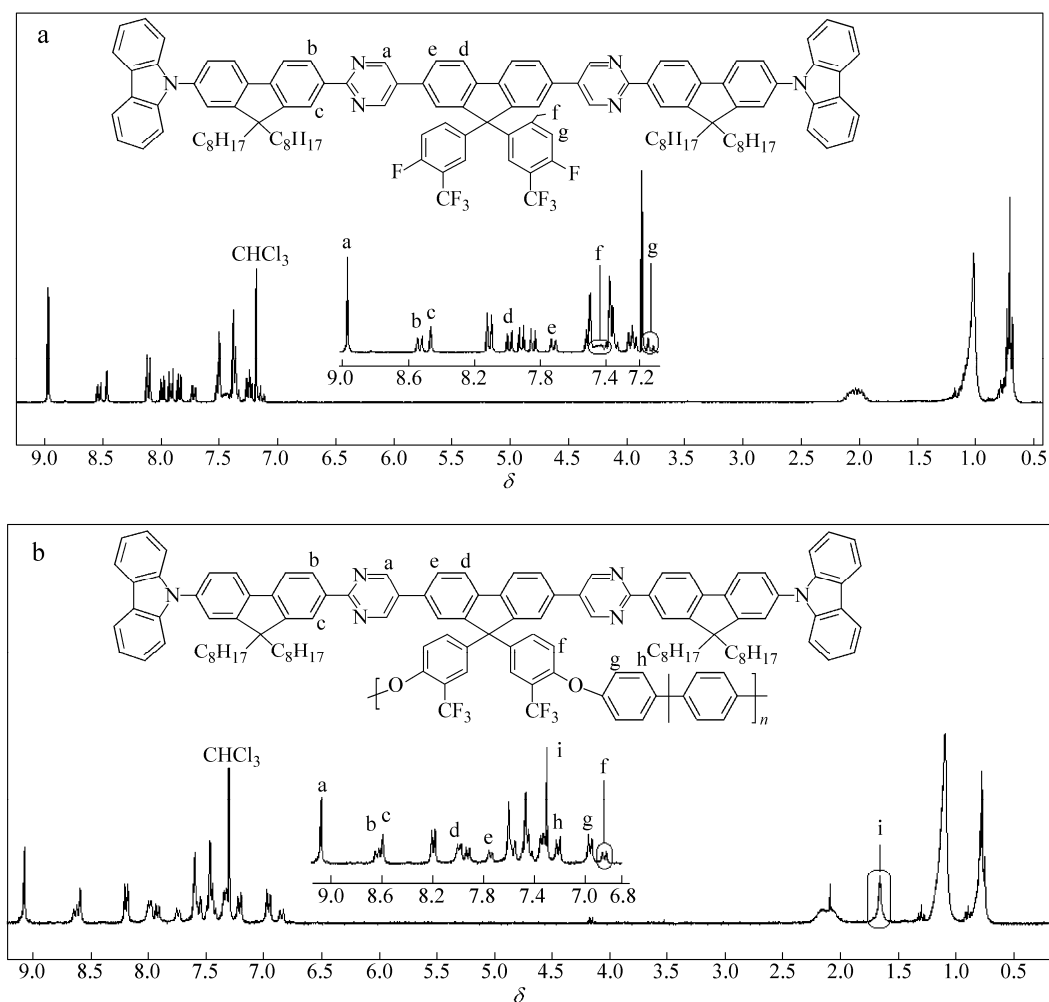


Fig. 1 ¹H-NMR spectra of **2Cz3F-Py** monomer (a) and its polymer **P2Cz3F-Py** (b)

Thermal Properties

Decomposition temperatures (T_d s) are evaluated by thermogravimetric analysis (TGA) with a scan rate of 10 K/min under nitrogen atmosphere. All the polymers exhibit T_d higher than 400 °C (Table 1), indicating that they are thermally stable. In addition, glass transition temperatures (T_g s) of the polymers are tested by differential scanning calorimetry (DSC). For comparison, T_g s of the monomers are also measured and listed in Table 2. From **3F-Py** to **2A3F-Py** and **2Cz3F-Py**, the T_g gradually increases from 69 °C to 96 °C and 102 °C. The same trend is also observed for **5F-Py**, **2A5F-Py** and **2Cz5F-Py**. This effect is reasonable when considering the larger volume of diphenylamine and carbazole units than hydrogen as well as the stronger rigidity of carbazole relative to diphenylamine. Similar to the monomers, T_g s of the polymers basically increase as the end-capper units alter from H to diphenylamine and carbazole, although for **P2A5F-Py** and **P2Cz5F-Py** the trend is reversed probably because of the much higher molecular weight of **P2A5F-Py** than **P2Cz5F-Py**. It should be noted that, by comparison to the corresponding monomers, all the polymers have much higher T_g s. For example, **P2A5F-Py** shows a T_g of 180 °C, which is 106 °C higher than that of **2A5F-Py**. This phenomenon may be attributed to the limitation of the movement of the pendants by the PAE main chain. The high T_g s of these polymers suggest that adopting the PAE main chain is an effective way to obtain morphologically stable materials.

Table 1. Weight-average molecular weight (M_w), polydispersity index (PDI), glass transition temperature (T_g), decomposition temperature (T_d), fluorescence quantum yield (Φ_{FL}), absorption and photoluminescence maxima ($\lambda_{abs, max}$ and $\lambda_{PL, max}$) of the polymers

Polymer	M_w $\times 10^{-4}$ ^a	PDI ^a	T_g (°C)	T_d (°C) ^b	Φ_{FL} ^c (%)	E_{ox} ^d (V)	E_{red} ^e (V)	$\lambda_{abs, max}$ (nm) ^f		$\lambda_{PL, max}$ (nm) ^g	
								Solution	Film	Solution	Film
P3F-Py	10.11	1.82	153	409	89	1.52	−1.94	366	366	407, 431	420, 435
P2Cz3F-Py	8.41	1.65	184	412	91	1.22	−1.90	293, 376	293, 376	423, 443	445
P2A3F-Py	5.31	1.71	182	409	63	0.93	−1.91	314, 408	315, 407	467	497
P5F-Py	9.12	1.73	140	411	88	1.49	−1.95	385	385	422, 443	436, 454
P2Cz5F-Py	8.16	1.41	171	412	86	1.25	−1.92	294, 386	295, 387	423, 447	437, 456
P2A5F-Py	28.12	2.08	180	402	72	0.97	−1.94	394	393	450	479

^a Measured by GPC using THF as solvent. The peaks of cyclomers were not included for calculation of M_w , and PDI. ^b Onset decomposition temperature measured by TGA under nitrogen. ^c Fluorescence quantum yield was measured in toluene with a chromophore concentration of 10^{-7} mol/L and 9,10-diphenylanthracene ($\Phi = 0.9$) as the standard. ^d Onset of the oxidation potentials. ^e Onset of the reduction potentials. ^f Solution spectra were measured in toluene with a repeat unit concentration of 10^{-6} mol/L; The films were spin cast from $CHCl_3$ solution with the concentration of 10 mg/mL. ^g The excitation wavelength for PL measurements is 360 nm.

Table 2. Glass transition temperature (T_g), absorption and photoluminescence maxima ($\lambda_{abs, max}$ and $\lambda_{PL, max}$) of the monomers

Compound	T_g (°C)	$\lambda_{abs, max}$ (nm) ^a	$\lambda_{PL, max}$ (nm) ^a	Φ_{FL} ^b (%)
3F-Py	69	367	406, 429	91
2Cz3F-Py	102	293, 377	424, 444	93
2A3F-Py	96	315, 412	468	65
5F-Py	61	382	422, 443	92
2Cz5F-Py	84	294, 386	424, 445	90
2A5F-Py	74	396	450	80

^a Solution spectra were measured in toluene with a concentration of 10^{-5} mol/L;

^b Fluorescence quantum efficiency was measured in toluene with a concentration of 10^{-7} mol/L and 9,10-diphenylanthracene ($\Phi = 0.9$) as the standard.

Optical Properties

The optical properties of the monomers in toluene solutions are firstly investigated, and the data are tabulated in Table 2. Compared with those without pyrimidine units^[32], all the pyrimidine-incorporated oligofluorenes here exhibit red-shifted absorption and photoluminescent (PL) spectra because of the existed ICT process. This ICT effect can be strengthened with the increasing electron donating capability in the order of hydrogen < carbazole

< diphenylamine, leading to the decrease of the bandgap. For instance, both the absorption and emission peaks are found to red shift from **3F-Py** to **2Cz3F-Py** and **2A3F-Py**. Furthermore, the π bridge length also has a significant influence on their optical properties. As for the hydrogen and carbazole end-capped monomers, the bifluorene bridge results in a bathochromic shift in both absorption and PL spectra due to the extended conjugation. However, as for the diphenylamine end-capped ones, a hypsochromic shift is observed with the increase of the bridge length. This is mainly because that the strong ICT character is greatly weakened when increasing the distance between the pyrimidine and diphenylamine moieties, which counteracts the accompanied conjugation extension effect.

As depicted in Fig. 2, the absorption and PL spectra of the polymers in toluene are almost the same as those of the monomers, suggesting that their optical properties are only determined by the oligofluorene pendants. On going from solutions to solid states, their PL spectra exhibit a red shift up to 30 nm (**P2A3F-Py**), originating from the much larger polarity of the excited state than the ground state in the D- π -A type oligofluorenes. With varying the bridge length and end-cappers, the emission color of the polymer films covers from deep blue for **P3F-Py** (420/435 nm) to light-blue for **P2A5F-Py** (479 nm) and greenish blue for **P2A3F-Py** (497 nm), which can be rationalized by the conjugation extension and ICT effect as discussed above. For **P3F-Py**, **P5F-Py** and **P2Cz5F-Py** films, the ratio of the emissive intensity at the shorter wavelength to that at the longer wavelength is lowered relative to the solutions because of the self absorption as observed in PFs. Additionally, the PL spectra of **P2A3F-Py** and **P2A5F-Py** show less resolved emission bands, probably attributed to the reduced rigidity of excited states induced by the introduction of diphenylamine groups. The PL quantum yields of the polymers are almost as high as those of the monomers, and all of them are above 60%, implying that these polymers are excellent candidates for PLEDs.

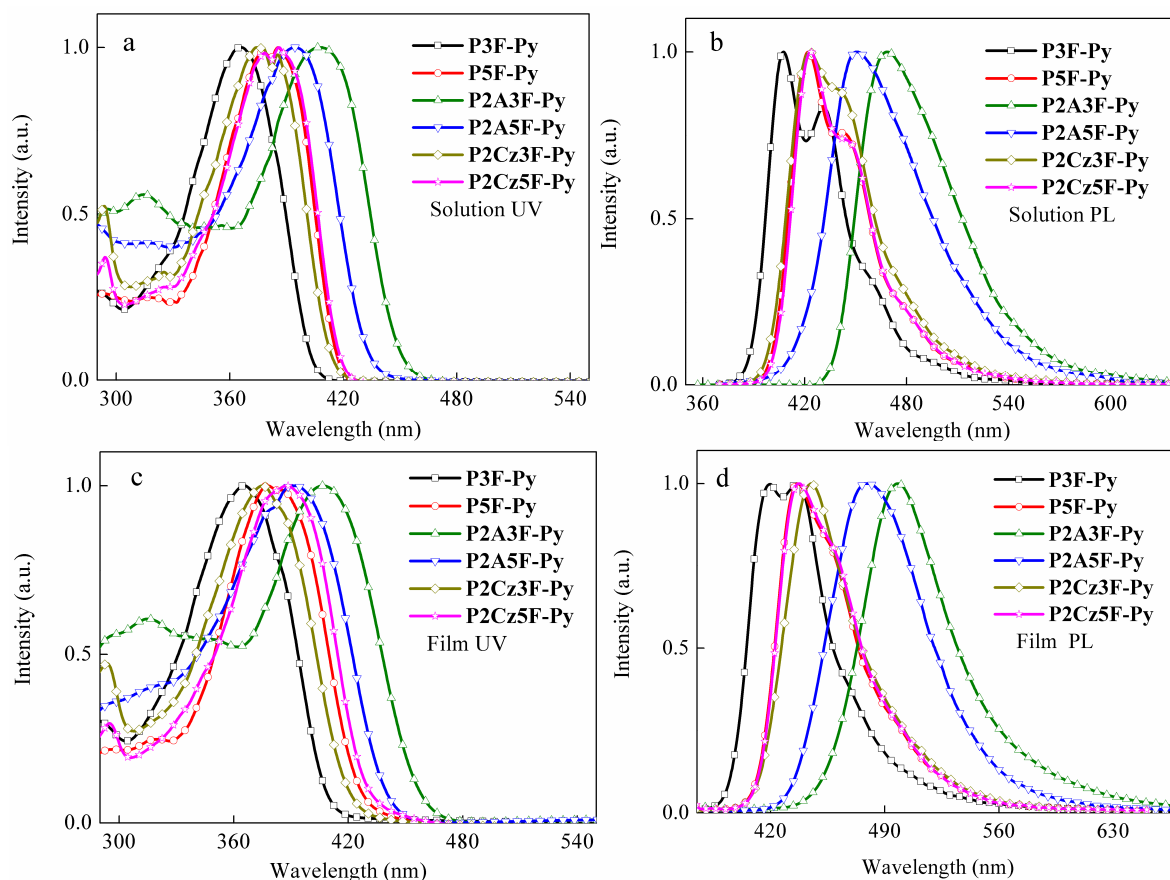


Fig. 2 Absorption and PL spectra of polymers in toluene solution (a and b) and in film state (c and d)

Electrochemical Properties

The electrochemical properties of the polymers are studied by means of cyclic voltammetry (CV) with a typical three-electrode cell, and their CV curves are shown in Fig. 3. From the onset of the oxidation and reduction potentials (see Table 1), the HOMO and LUMO energy levels of the polymers can be estimated. The polymers **PnF-Py** ($n = 3$ or 5) show the HOMO levels of -5.8 to -5.9 eV, identical to the corresponding oligofluorene^[33–35], indicating that the pyrimidine units do not involve in the oxidation processes. The polymers **P2AnF-Py** and **P2CznF-Py** ($n = 3$ or 5) exhibit the first oxidation waves at 0.9 and 1.2 V, respectively, corresponding to the diphenylamine and carbazole units. And the HOMO levels are calculated to be -5.3 and -5.6 eV for **P2AnF-Py** and **P2CznF-Py** ($n = 3$ or 5), respectively. For all the polymers, the LUMO levels are at around -2.5 eV, which is 0.4 eV lower than those of the oligofluorenes without pyrimidine groups. This is caused by the electron-deficient feature of pyrimidine. We note that, although the polymers are end-capped with different substituents, their LUMO levels nearly keep unchanged. Therefore, the HOMO and LUMO levels can be tuned independently as reported in previous paper^[23], which is beneficial for the fine design of materials used for PLEDs.

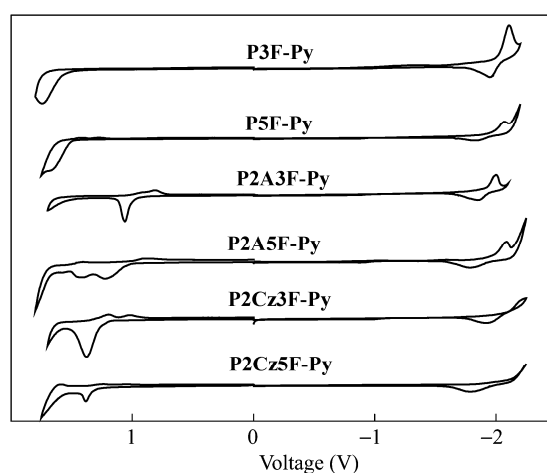


Fig. 3 Cyclic voltammograms of the polymers versus Ag/AgCl

Device Properties

PLEDs have been fabricated with a configuration of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (50 nm)/Polymer (80 nm)/Ca (10 nm)/Al (200 nm). The EL spectra of the polymers are presented in Fig. 4, close to their PL ones in film states. **P3F-Py** and **P5F-Py** show deep blue emission with Commission Internationale de L'Eclairage (CIE) coordinates of (0.17, 0.12–0.13), **P2A5F-Py** shows light-blue emission with CIE coordinates of (0.19, 0.29), while **P2A3F-Py** with stronger ICT character shows greenish blue emission with CIE coordinates of (0.32, 0.47). Figure 5 depicts the luminous efficiency versus voltage curves of the devices, and the device performance is summarized in Table 3. **P3F-Py** exhibits a turn-on voltage of 7 V, which is lowered by 3 V relative to the analogue without pyrimidine units. This is because that the incorporation of pyrimidine can favor electron injection by reducing the LUMO levels. For **P5F-Py**, the turn-on voltage decreases to 6 V, and the maximum luminous efficiency reaches to 0.5 cd/A, indicating the important role of conjugation extension upon improving device properties. By incorporating carbazole and diphenylamine end-cappers, the turn-on voltage further reduces to 5 V because of the elevated HOMO levels and thus lowered hole-injection barriers. Moreover, the maximum brightness and luminous efficiency of **P2AnF-Py** and **P2CznF-Py** are distinctly improved compared with **PnF-Py** ($n = 3$ or 5). For example, **P2A3F-Py** displays a maximum brightness of 2864 cd/m² and maximum luminous efficiency of 1.35 cd/A, which is 47 and 22-fold higher than those of **P3F-Py**, respectively. The improvement can be ascribed to the much more balanced carrier-injection induced by the bipolar feature of the chromophores. Besides this reason, the emission shift toward greenish blue

zone that is much more sensitive to the human eyes also contributes to the enhanced device performance of **P2A3F-Py**. Among these polymers, **P2Cz5F-Py** has excellent trade-off between the efficiency and emission wavelength, realizing a peak luminous efficiency as high as 1.26 cd/A with CIE coordinates of (0.17, 0.17).

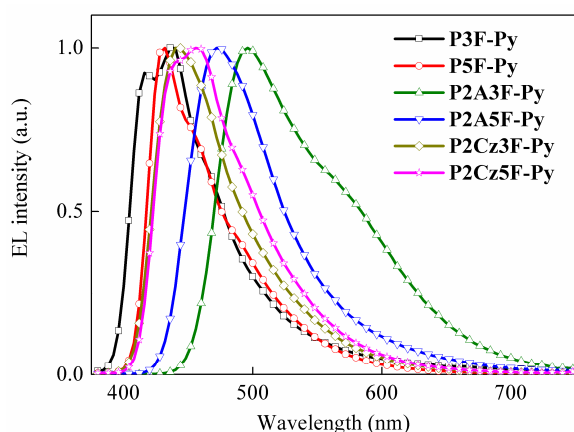


Fig. 4 EL spectra of the polymers with device structure of ITO/PEDOT/Polymers/Ca/Al

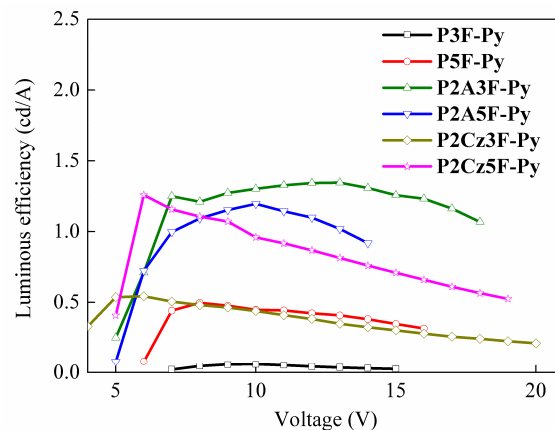


Fig. 5 Luminous efficiency-voltage relationship of the devices based-on the polymers

Table 3. Device performance of the polymers

Polymer	$\lambda_{\text{EL,max}}$ (nm)	V_{on}^a (V)	L_{max} (cd/m ²)	LE (cd/A)	CIE (x, y)
P3F-Py	416, 438	7	60	0.06	0.17, 0.12
P2Cz3F-Py	442	5	1329	0.54	0.17, 0.15
P2A3F-Py	496	5	2864	1.35	0.32, 0.47
P5F-Py	430	6	624	0.50	0.17, 0.13
P2Cz5F-Py	442, 455	5	1493	1.26	0.17, 0.17
P2A5F-Py	472	5	3196	1.20	0.19, 0.29

^aThe voltage at the brightness of 1 cd/m²

CONCLUSIONS

By tuning the π bridge length and the end-cappers' electron-donating capability, we have designed and synthesized a series of blue light-emitting PAEs containing bipolar oligofluorene pendants embedded with electron deficient pyrimidine units. It is found that, the increase of the bridge length from monofluorene to bifluorene can extend the conjugation accompanied by the weakness of the ICT effect, whereas changing the end-cappers from hydrogen to carbazole and diphenylamine can enhance this ICT character. As a result, the emission color of these polymers is adjusted from deep-blue to greenish blue, and their HOMO and LUMO levels are also modulated to favor charge injection at the same time. An excellent trade-off between the efficiency and emission wavelength has been realized for **P2Cz5F-Py** with bifluorene bridge and carbazole end-capper. It shows a peak luminous efficiency as high as 1.26 cd/A with CIE coordinates of (0.17, 0.17). The results indicate that endowing PAE-based blue light-emitting polymers with the bipolar nature is a promising approach to improve their device performance.

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