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Conjugated polymers containing trifluoren-2-ylamine, trifluoren-2-ylbenzene and trifluoren-2-yltriazine for electroluminescence

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ABSTRACT

A series of light-emitting conjugated polymers (LEPs) based on building blocks of electron-donating trifluoren-2-ylamine (TFA), electrically neutral 1,3,5-trifluoren-2-ylbenzene (TFB), and electronwithdrawing 2,4,6-trifluoren-2-yltriazine (TFT) were successfully synthesized via palladium-catalyzed Suzuki cross-coupling polycondensation. Their structure-property relationships were thoroughly studied. For P1 containing electron-withdrawing backbone and electron-donating pendants, their photophysical properties in solution are strongly dependent on the solvent polarity due to the intense intramolecular charge-transfer (ICT) interaction. In addition, their emission colors and energy levels could be effectively tuned by changing the structure of the main chain as well as the substituent at the pendent fluorene of TFT, TFB, and TFA. To evaluate their electroluminescence properties, double-layer devices with a configuration of ITO/PEDOT:PSS (40 nm)/emitting layer (EML) (70-80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al were fabricated, where the developed polymers were used as an EML and TPBI (2,2',2"-(1,3,5-benzenetriyl)-tris-(1-phenyl-1H-benzimidazole)) was used as an electron-transport and hole-block layer. Deep-blue light emission was achieved for the device based on P1d, a polymer based on TFT and the second generation (G2) of carbazole dendrimer pendant, that shows a maximum current efficiency (CE) of 1.26 cd A^{-1} , corresponding to external quantum efficiency (EQE) of 1.27%, with Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.14). In comparison, due to the intense ICT interaction between the main chain and the side chain, light-green emission was achieved for the device based on P1c, a polymer based on TFT and bis(9,9-dioctyl-9H-fluoren-2-yl)amine pendant, giving the highest maximum CE of 4.10 cd A^{-1} , corresponding to EQE of 2.45%, with CIE coordinates of (0.24,0.51), although either of the main chain and the side chain emits blue light.

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1. Introduction

Over the last two decades, design and synthesis of light-emitting conjugated polymers (LEPs) as the active materials in polymer light-emitting diodes (PLEDs) have been the subject of intense academic and industrial research due to their great potential applications in full-color flat-panel displays, back-lighting sources for liquid-crystal displays, and next-generation solid-state lighting sources [1–6]. Enormous efforts have been focused on their luminescence properties through molecular engineering [7]. It is well-known that the emission color obviously depends upon the energy band gap between the highest occupied molecular orbital (LUMO) energy levels of the chromophore. If two chromophores with

0032-3861/\$ — see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2012.11.050 different energy band gaps are mixed together, energy transfer occurs from the chromophore with the larger energy band gap to that with the smaller energy band gap, and emission from the latter dominates [8]. In view of this effect, one method for color-tuning is to blend a dye chromophore into a host. Doping the host with highly fluorescent dyes has been proven to be an efficient strategy to achieve high color purity of emission color and to increase the efficiency of the devices [9,10]. Zhen et al. achieved pure blue emission with extremely high maximum external quantum efficiency (EQE) of 9.40% and Commission Internationale de l'Eclairage (CIE) coordinates of (0.147, 0.139) by doping the emitter into a small molecular host material of 4,4'-bis(carbazol-9-yl)biphenyl (CBP) [10]. However, the blend system like this tends to show phase separation during the device operation and over time, and thus leads to instability in the device performance [11]. An alternative solution is to covalently attach the dye chromophore to the polymer which could effectively prevent the aggregation of the dye chromophore caused by the migration of dye inside the polymer matrix





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[12,13]. In addition, this approach facilitates the efficient energy transfer from the polymer matrix to the dye chromophore and easily confines the excitons to the chromophore [14], which acts as an effective energy trap for excitons formed at the higher-energy segments of the polymer matrix [15]. Significant efforts have been made to tune the emission colors of the fluorene-based polymers (PFs), in which fluorene, its oligomers, or polymers could be used as the high energy chromophore segments because of their large energy band gaps to generate other colors at longer wavelengths by efficient energy transfer to the low-energy chromophore units. For example, Ego et al. reported the emission color of PFs can be facilely tuned across the whole visible spectrum through efficient energy transfer to the chromophore units by incorporation of perylene dyes in the polymer main chain, at the chain termini, or as side chains [12]. Wang and co-workers designed and synthesized three kinds of red electroluminescent (EL) polymers based on PF as the main chain and the low-energy chromophore of 2,1,3-benzothiadiazole derivatives with different emission wavelengths as red chromophore units on the side chain [16]. So far, most of the color-tunable PFs have been developed through the approach of energy transfer by incorporating low-energy band gap co-monomers into the main chain or attaching dyes as pendent side groups [12-14,16]. Pu et al. developed four fluorescent dyes of bis(difluorenyl) amino-substituted carbazole, pyrene, perylene, and benzothiadiazole derivatives, and their emitting colors could be tuned from sky blue to deep red [17]. Very recently, we successfully designed and synthesized a series of blue light-emitting conjugated polymers based on electrondonating trifluoren-2-vlamine (TFA) as a building block and their emission colors could be effectively tuned in the region of deep-blue with CIE coordinates of (0.16, 0.12) and light-blue with CIE coordinates of (0.18, 0.30) by introducing various substituents onto the TFA as the pendants [18], indicating that color-tuning of the conjugated polymers can be also achieved by controlling the effective conjugation length and introducing intramolecular charge-transfer (ICT) interaction.

In this article, a series of LEPs based on building blocks of electron-donating TFA, electrically neutral 1,3,5-trifluoren-2ylbenzene (TFB), and electron-withdrawing analogue of 2,4,6trifluoren-2-yltriazine (TFT) were designed and synthesized as active materials of PLEDs. Among the three fluorene arms of these building blocks, two fluorene arms combine with another fluorene unit to be the main chain of the polymer, and the other one fluorene arm acts as the side chain. The structures of the main chains of all the polymers are nearly identical except for the distinct junctions of the side chains to the backbones, changing from electron-donating amine, to electrically neutral benzene, and electron-withdrawing triazine. Moreover, substituted groups of electron-donors, like carbazole, 3,6-di-tert-butyl carbazole, the second generation (G2) of carbazole dendrimer, and bis(9,9-dioctyl-9H-fluoren-2-yl) amine, were introduced onto the pendent fluorene as the side chain. Their structure-property relationships were thoroughly studied. As expected, their energy levels could be effectively tuned by changing the junctions of the side chains to the backbones and the pendent electron-donors. More importantly, this paper offers an alternative approach to tune the emission color of LEPs by introducing different building blocks from electron-acceptor to electron-donor as the main chain and thus the ICT interaction between the side chain and the main chain.

2. Experimental

2.1. Materials

All reagents were obtained from Sigma Aldrich Chemical Co., Alfa Aesar Chemical Co., Aladdin Chemical Co., and HuiCheng Chemical Co., and they were used as received unless otherwise specified. All manipulations involving air-sensitive reagents were performed in the atmosphere of dry argon. The solvents were purified by routine procedure and distilled under dry argon before being used. 2-Dibromo-9,9-dioctylfluorene (1) [19], 2-amimo-9,9-dioctylfluorene (2) [18], 7-bromo-9,9-dioctyl-9H-fluorene-2-carbonitrile (4) [20], 3,6-di-*tert*-butyl-9H-carbazole (7) [21], 3,6-di-tert-butyl-9(-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-6-yl)-9H-carbazole (8) [21], 13a [18], 13b [18], and 2,7-bis(4,4,5,5-tramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (14) [22] were prepared according to the reference procedures.

2.1.1. Synthesis of bis(9,9-dioctyl-9H-fluoren-2-yl)amine (3)

A mixture of tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃) (98 mg, 0.11 mmol), diphenylphosphino-ferrocene (DPPF) (228 mg, 0.41 mmol), **1** (1.89 g, 4.03 mmol), **2** (1.63 g, 4.02 mmol), and *t*-BuOK (1.68 g, 14.97 mmol) was stirred in toluene (40 ml) for 24 h at 110 °C under an argon atmosphere. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic extracts were combined and washed with brine and dried with anhydrous MgSO₄. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give a brown viscous liquid 2.00 g. Yield: 62.6%. ¹H NMR (300 MHz, DMSO), δ (ppm): 8.52 (s, 1H), 7.66 (t, 4H), 7.35 (d, 2H), 7.30–7.20 (m, 6H), 6.91 (d, 2H), 2.00–1.70 (m, 8H), 1.30–1.00 (m, 40H), 0.80–0.75 (t, 12H), 0.70–0.40 (m, 8H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 137.87, 129.05, 128.24, 126.38, 125.32, 55.00, 40.64, 35.47, 31.84, 30.21, 29.73, 29.36, 29.33, 23.90, 22.63, 21.46, 14.09.

2.1.2. Synthesis of 2,4,6-tris(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-[1,3,5]triazine (**5**)

Under a nitrogen atmosphere, a solution of 4 (8.95g, 18.1 mmol) in 50 ml anhydrous chloroform (CHCl₃) was added dropwise into the trifluoromethanesulfonic acid at 0 °C, then the mixture was warmed to room temperature and stirred for 2 days. The reaction was guenched with a solution of 6 ml ammonia monohydrate in 100 ml water, and the mixture was extracted with chloroform. The extract was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give a yellow solid (8.95 g) in 97.2% yield. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.83 (d, 3H), 8.73 (s, 3H), 7.90 (d, 3H), 7.69 (d, 3H), 7.60-7.50 (m, 6H), 2.19-2.00 (m, 12H), 1.20–1.00 (m, 60H), 0.80–0.60 (m, 10H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 171.81, 154.12, 150.79, 144.47, 139.34, 135.84, 135.67, 130.25, 128.46, 126.42, 123.32, 122.26, 121.85, 119.88, 67.96, 55.64, 40.24, 31.77, 29.97, 29.70, 29.20, 25.61, 23.80, 22.58, 14.01. Calcd C₉₀H₁₂₀N₃Br₃ 1483.6, EI-MS (*m*/*z*): 1482.7 (M⁺).

2.1.3. Synthesis of 9-{7-[4,6-bis(7-bromo-9,9-dioctyl-9H-fluoren-2yl)-[1,3,5]triazin-2-yl]-9,9- dioctyl-9H-fluoren-2-yl}-9H-carbazole (**9a**)

Under an argon atmosphere, a mixture of carbazole (84 mg, 0.5 mmol), **5** (0.74 g, 0.5 mmol), Cul (0.49 g, 2.57 mmol), K₂CO₃ (0.49 g, 3.55 mmol), and 18-crown-6 (90 mg, 0.34 mmol) in 3.2 ml o-dichlorobenzene was heated to 180 °C and stirred for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane. The extract was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give yellow-green solid (0.326 g) in 41.6% yield. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.92–8.88 (d, 1H), 8.87–8.83 (d, 2H), 8.80 (s, 1H), 8.75 (s, 2H), 8.21–8.18 (d, 2H), 8.08–8.00 (t, 2H), 7.95–7.90 (d, 2H), 7.78–7.68 (m, 3H), 7.65–7.59 (m, 2H), 7.58–7.55 (m, 2H), 7.54–7.50 (m, 1H), 7.49–7.42 (m, 4H), 7.38–7.30 (m, 2H),

2.23–2.00 (m, 12H), 1.30–1.00 (m, 60H), 0.90–0.60 (m, 30H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 171.83, 154.28, 154.14, 153.85, 151.49, 150.83, 150.62, 144.79, 144.59, 144.52, 140.98, 139.97, 139.53, 139.35, 137.39, 136.15, 135.84, 135.66, 135.54, 132.35, 130.27, 128.49, 126.43, 126.01, 123.49, 123.33, 122.30, 122.21, 121.91, 121.77, 120.46, 120.04, 109.81, 93.99, 55.67, 55.59, 40.30, 31.81, 30.07, 30.00, 29.74, 29.35, 29.25, 24.10, 23.83, 22.62, 14.07.

2.1.4. Synthesis of 9-{7-[4,6-bis(7-bromo-9,9-dioctyl-9H-fluoren-2yl)-[1,3,5]triazin-2-yl]-9,9- dioctyl-9H-fluoren-2-yl}-3,6-di-tertbutyl-9H-carbazole (**9b**)

9b was synthesized by following the similar procedure of **9a**. Yield: 42.5%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.91–8.86 (m, 2H), 8.84 (s, 1H), 8.79 (s, 1H), 8.75 (s, 2H), 8.19 (d, 2H), 8.04-7.98 (t, 2H), 7.93-7.90 (d, 2H), 7.76 (s, 1H), 7.71 (s, 1H), 7.68 (s, 1H), 7.63–7.54 (m, 5H), 7.52 (d, 1H), 7.49 (d, 1H), 7.45–7.42 (m, 2H), 2.18–2.00 (m, 12H), 1.49 (s, 18H), 1.30–1.00 (m, 60H), 0.90–0.60 (m, 30H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 171.88, 171.81, 154.14, 153.73, 151.44, 150.81, 144.95, 144.49, 142.98, 139.97, 139.36, 139.26, 139.01, 137.91, 135.69, 135.37, 130.26, 128.50, 126.43, 125.51, 123.65, 123.49, 123.33, 122.28, 121.89, 121.68, 121.51, 119.94, 116.39, 109.25, 55.67, 55.63, 40.29, 34.79, 32.06, 31.88, 31.81, 30.06, 30.00, 29.73, 29.37, 29.31, 29.25, 26.94, 24.06, 23.82, 22.62, 14.07.

2.1.5. Synthesis of 7-(4,6-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-1,3,5-triazin-2-yl)-N,N-bis(9,9-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-amine (**9c**)

9c was synthesized by following the similar procedure of **3**. Yield: 44.4%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.85–8.80 (m, 3H), 8.74–8.70 (m, 3H), 7.96–7.80 (m, 3H), 7.71–7.50 (m, 9H), 7.42–7.28 (m, 10H), 7.25–7.23 (m, 1H), 7.10–7.02 (m, 3H), 2.20–1.80 (m, 20H), 1.30–1.00 (m, 100H), 0.90–0.50 (m, 50H).

2.1.6. Synthesis of 9-{7-[4,6-bis(7-bromo-9,9-dioctyl-9H-fluoren-2yl)-[1,3,5]triazin-2-yl]-9,9- dioctyl-9H-fluoren-2-yl}-3,6-di-tertbutyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-6-yl)-9H-carbazole (**9d**)

9d was synthesized by following the similar procedure of **9a**. Yield: 34.3%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.95–8.92 (d, 1H), 8.88 (s, 1H), 8.86–8.84 (m, 2H), 8.76 (s, 2H), 8.29 (s, 2H), 8.18 (s, 5H), 8.09–8.06 (d, 1H), 7.94–7.92 (d, 2H), 7.81 (s, 2H), 7.73–7.68 (m, 4H), 7.66–7.62 (m, 2H), 7.56 (s, 3H), 7.53 (s, 1H), 7.50 (s, 1H), 7.48 (s, 3H), 7.39 (s, 3H), 7.36 (s, 1H), 2.30–2.00 (m, 12H), 1.48 (s, 36H), 1.30–1.00 (m, 60H), 0.90–0.60 (m, 30H).

2.1.7. Synthesis of 1-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl) ethanone (**10**)

Under a nitrogen atmosphere, a solution of **1** (10.22 g, 22.0 mmol) and anhydrous aluminum chloride (AlCl₃) in 80 ml dichloromethane (CHCl₂) was cooled to 0 °C. Then CH₃COCl (1.62 ml, 22.9 mmol) was added via syringe, the mixture was stirred for 12 h at 0 °C. The reaction was quenched with 2% NaOH solution. The reaction mixture was extracted with ethyl acetate. The organic extracts were combined and washed with brine and dried with anhydrous MgSO₄. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give a yellow solid 9.36 g. Yield: 83.9%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.95 (m, 1H), 7.94 (m, 1H), 7.72 (m, 1H), 7.61 (m, 1H), 7.47–7.5 (m, 2H), 2.66 (s, 3H), 1.93–2.02 (m, 4H), 1.02–1.11 (m, 20H), 0.76 (m, 6H), 0.53–0.59 (m, 4H).

2.1.8. Synthesis of 1,3,5-tris(7-bromo-9,9-dioctyl-9H-fluoren-2-yl) benzene (11)

Under an argon atmosphere, silicon tetrachloride $(SiCl_4)$ was added dropwise into the solution of **10** (6 g, 11.8 mmol) in 80 ml

ethanol. The mixture was stirred for 18 h at room temperature and was then poured into water and extracted with dichloromethane. The extract was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give glassy solid (3.57 g) in 60.1% yield. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.87 (s, 3H), 7.72–7.81 (m, 6H), 7.67 (m, 3H), 7.59–7.62 (m, 3H), 7.43–7.49 (m, 6H), 1.91–2.08 (m, 12H), 0.98–1.39 (m, 60H), 0.77–0.92 (m, 18H), 0.62–0.67 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 153.22, 151.26, 142.84, 140.52, 139.73, 130.08, 126.48, 126.27, 125.25, 121.76, 121.20, 121.15, 120.13, 55.62, 40.32, 31.75, 29.97, 29.18, 23.77, 22.58, 14.03. Calcd C₉₃H₁₂₃Br₃ 1480.7, EI-MS (*m/z*): 1480.0 (M⁺).

2.1.9. Synthesis of 9-{7-[3,5-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)phenyl]-9,9-dioctyl-9H- fluoren-2-yl}-9H-carbazole (**12a**)

12a was synthesized by following the similar procedure of **9a**. Yield: 34.7%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.19 (d, 2H), 7.98– 7.87 (m, 5H), 7.83–7.65 (m, 10H), 7.64–7.53 (m, 3H), 7.52–7.40 (m, 7H), 7.50–7.28 (m, 2H), 2.10–1.09 (m, 12H), 1.03–1.00 (m, 60H), 0.90–0.60 (m, 30H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 140.75, 140.57, 140.46, 140.38, 140.02, 139.82, 139.75, 136.56, 136.00, 132.20, 130.10, 126.52, 126.29, 125.93, 125.31, 123.43, 121.93, 121.87, 121.74, 121.53, 121.22, 120.95, 120.39, 120.28, 120.20, 119.90, 109.81, 92.68, 55.65, 55.58, 40.31, 31.77, 30.05, 29.98, 29.71, 29.30, 29.20, 24.06, 23.79, 22.61, 14.05.

2.1.10. Synthesis of 9-{7-[3,5-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)phenyl]-9,9-dioctyl-9H- fluoren-2-yl}-3,6-di-tert-butyl-9Hcarbazole (**12b**)

12b was synthesized by following the similar procedure of **9a**. Yield: 39.4%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.18 (s, 2H), 7.96– 7.87 (m, 5H), 7.83–7.74 (m, 5H), 7.73 (s, 1H), 7.68 (s, 2H), 7.63 (s, 1H), 7.60 (s, 1H), 7.58–7.54 (m, 2H), 7.52–7.45 (m, 6H), 7.42–7.39 (m, 2H), 2.10–1.09 (m, 12H), 1.51 (s, 18H), 1.03–1.00 (m, 60H), 0.90– 0.60 (m, 30H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 153.24, 152.73, 151.92, 151.28, 142.94, 142.87, 142.83, 140.58, 140.27, 140.17, 139.75, 139.48, 139.35, 137.04, 130.10, 126.54, 126.27, 125.45, 125.33, 123.60, 126.40, 121.80, 121.49, 121.22, 120.88, 120.18, 116.36, 109.25, 55.65, 55.61, 40.37, 34.78, 32.07, 31.87, 31.80, 30.07, 30.01, 29.74, 29.35, 29.31, 29.24, 26.94, 24.03, 23.80, 22.64, 14.11.

2.1.11. Synthesis of 7-(3,5-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)phenyl)-N,N-bis(9,9-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-amine (**12c**)

12c was synthesized by following the similar procedure of **9a**. Yield: 31.1%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.92–7.85 (m, 3H), 7.82–7.72 (m, 6H), 7.71–7.64 (m, 5H), 7.63–7.53 (m, 6H), 7.52–7.42 (m, 3H), 7.35–7.27 (m, 8H), 7.25–7.20 (m, 1H), 7.08–7.01 (d, 3H), 2.10–1.08 (m, 20H), 1.04–1.00 (m, 100H), 0.90–0.50 (m, 50H). ¹³C NMR (CDCl₃, 75 MHz), δ (ppm): 151.04, 150.42, 142.77, 141.00, 140.82, 140.64, 140.39, 139.73, 135.96, 132.17, 130.06, 126.77, 126.48, 126.26, 125.20, 122.74, 121.72, 121.50, 121.16, 120.30, 120.16, 119.01, 92.61, 55.62, 55.55, 55.33, 55.10, 40.42, 40.33, 38.98, 34.14, 31.85, 31.75, 30.13, 29.96, 29.70, 29.44, 29.30, 29.18, 23.99, 23.76, 22.64, 22.59, 20.15, 19.17, 14.39, 14.09, 14.03, 11.37.

2.1.12. General procedure for polymer synthesis

Carefully purified **14** (0.5 mmol), 0.5 mmol **9a** or **9b** or **9c** or **9d** or **12a** or **12b** or **12c**, Pd(OAc)₂ (3 mg), tricyclohexyl phosphine (P(Cy)₃) (6 mg), 1 ml Et₄NOH and 1 ml deionized water were dissolved in 8–15 ml toluene. The mixture was heated to 90–100 °C with vigorous stirring for 48 h under an argon atmosphere. At the end of polymerization, polymers were sequentially end-capped with phenylboronic acid and bromobenzene in order to avoid

a carrier trap and luminescence quenching center formation by end groups in OLEDs [23]. The mixture was then poured into methanol. The precipitated material was recovered by filtration and was extracted with methanol and acetone utilizing a Soxhlet extractor to remove oligomers and catalyst residues. The resulted polymers were dried under vacuum. Yields: 50–80%.

2.1.12.1. **P1a**. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.98–8.88 (m, 3H), 8.87–8.80 (m, 3H), 8.21 (d, 2H), 8.10–7.86 (m, 8H), 7.80–7.60 (m, 10H), 7.52–7.46 (m, 3H), 7.44–7.40 (m, 1H), 7.38–7.31 (m, 2H), 2.40–2.00 (m, 16H), 1.30–1.00 (m, 80H), 0.97–0.70 (m, 40H). Anal. Calcd. for [C₁₃₁H₁₆₈N₄]_n: C, 87.47; H, 9.41; N, 3.11. Found: C, 85.90; H, 10.16; N, 2.93.

2.1.12.2. **P1b.** ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.97–8.82 (m, 6H), 8.19 (s, 1H), 8.10–7.83 (m, 9H), 7.79–7.68 (m, 7H), 7.66–7.60 (m, 2H), 7.53–7.42 (m, 5H), 2.40–2.00 (m, 16H), 1.50 (s, 18H), 1.30–1.00 (m 80H), 0.99–0.70 (m, 40H). Anal. Calcd. for [C₁₃₉H₁₈₄N₄]_n: C, 87.36; H, 9.71; N, 2.93. Found: C, 84.97; H, 7.85; N, 2.63.

2.1.12.3. **P1c**. ¹H NMR (300 MHz, CDCl₃), δ (ppm): ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.92–8.71 (m, 6H), 8.02–7.45 (br, 20H), 7.44–7.28 (br, 9H), 7.23–7.14 (m, 3H), 2.30–1.80 (m, 24H), 1.40–0.92 (m, 120H), 0.90–0.40 (m, 60H). Anal. Calcd. for [C₁₇₇H₂₄₂N₄]_n: C, 87.64; H, 10.06; N, 2.31. Found: C, 85.54; H, 11.02; N, 2.11.

2.1.12.4. **P1d.** ¹H NMR (300 MHz, CDCl₃), δ (ppm): 9.01–8.81 (br, 6H), 8.29 (s, 2H), 8.18 (s, 5H), 8.12–7.88 (br, 6H), 7.84–7.60 (m, 15H), 7.51–7.47 (d, 4H), 7.40–7.37 (d, 4H), 2.40–2.00 (m, 16H), 1.55 (s, 36H), 1.30–1.00 (m, 80H), 0.95–0.60 (m, 40H). Anal. Calcd. for [C₁₇₁H₂₁₄N₆]_n: C, 87.26; H, 9.16; N, 3.57. Found: C, 83.97; H, 10.33; N, 3.29.

2.1.12.5. **P2a**. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.19 (d, 2H), 8.00–7.65 (m, 24H), 7.62–7.56 (m, 2H), 7.51–740 (m, 4H), 7.39–7.30 (m, 3H), 2.30–2.00 (m, 16H), 1.30–1.00 (m, 80H), 0.95–0.60 (m, 40H). Anal. Calcd. for [C₁₃₄H₁₇₁N]_n: C, 89.62; H, 9.60; N, 0.78. Found: C, 87.30; H, 10.13; N, 0.75.

2.1.12.6. **P2b.** ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.18 (s, 2H), 7.97 (s, 3H), 7.96–7.66 (m, 21H), 7.60–7.55 (m, 2H), 7.51 (s, 1H), 7.49–7.43 (m, 3H), 7.41 (s, 1H), 2.30–2.00 (m, 16H), 1.49 (s, 18H), 1.30–1.00 (m, 80H), 0.97–0.70 (m, 40H). Anal. Calcd. for [$C_{142}H_{187}N$]_n: C, 89.39; H, 9.88; N, 0.73. Found: C, 87.37; H, 10.47; N, 0.71.

2.1.12.7. **P2c**. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.00–7.50 (m, 31H), 7.45–7.28 (br, 10H), 2.20–1.80 (m, 24H), 1.30–1.00 (m, 120H), 0.90–0.50 (m, 60H). Anal. Calcd. for [C₁₈₀H₂₄₅N]_n: C, 89.23; H, 10.19; N, 0.58. Found: C, 86.48; H, 10.66; N, 0.70.

2.2. Measurement and characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-300 (300 MHz) in deuterated chloroform (CDCl₃) with tetramethylsilane as an internal reference. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by a Waters GPC 2410 in THF using a calibration curve with standard polystyrene as a reference. Elemental analysis was performed on a Vario EL elemental analysis instrument (Elementar Co.). Differential scan calorimetry (DSC) measurements were performed on a Netzsch DSC 204 under N₂ flow at a heating rate of 10 °C min⁻¹ and a cooling rate of 20 °C min⁻¹. Thermogravimetric analysis (TGA) measurements were performed on a Netzsch TG 209 under N₂ flow at a heating rate of 10 °C min⁻¹. UV–vis absorption spectra were recorded on an HP 8453 spectrophotometer. Photoluminescent (PL) spectra were measured using a Jobin-Yvon spectrofluorometer. PL quantum efficiencies were determined on a fluoyo SENS spectrofluorometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a platinum working electrode and a platinum wire counter electrode at a scan rate of 50 mV s⁻¹ against a Ag/Ag⁺ reference electrode with an argon saturated anhydrous solution of 0.1 mol L⁻¹ tetrabuty-lammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. The polymer films for electrochemical measurements and PL quantum efficiencies measurements were coated from their toluene solutions.

2.3. Device fabrication and characterization

The fabrication process of the devices is as the following. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, detergent, and isopropyl alcohol sequentially. After treatment with oxygen plasma, a 40-nm-thin layer of poly-(3,4-ethylenedioxythiopene) : poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron P 4083) was spincoated as a buffer layer. After being dried in a vacuum oven at 80 °C for 12 h, the xylene solutions of the polymers prepared in a nitrogen-filled drybox were spin-coated on the top of the PEDOT:PSS film. The thickness of the spin-coated film was controlled by regulating the spinning speed and the solution concentration, measured with an Alfa Step 500 surface profiler (Tencor). The low mass materials were vacuum deposited in a vacuum of 1×10^{-4} Pa. A thin layer of CsF (1.5 nm) and subsequently 120-nm-thin layer of Al were vacuum deposited in a vacuum of 1×10^{-4} Pa as the cathode. Device performances were measured inside a drybox. Current versus driving voltage characteristics were recorded with a Keithley 236 source meter. Electroluminescent (EL) spectra were obtained by Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (Photo Research). External quantum efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

3. Results and discussion

3.1. Synthesis and chemical characterization

In order to tune the HOMO and LUMO energy levels of the polymers to facilitate carrier injection from the electrode and thus the carrier balance in the emissive layer (EML), various electrondonating substituents, such as carbazole (6), 3,6-di-tert-butyl carbazole (7), and bis(9,9-dioctyl-9H-fluoren-2-yl)amine groups (3) were introduced onto the pendent fluorene as the side chain for LEPs of P1 and P2 based on TFT and TFB, respectively. In addition, the bulky pendant of G2 carbazole dendrimer (8) was also introduced onto the pendent fluorene of TFT to give **P1d**. Although great effort was made to introduce 3 and 8 onto TFA, it was proved to be futile finally. It was suspected that the electron-donating property of TFA is unfavorable to cuprous iodide or copper powder catalyzed Ullmann coupling reaction and palladium-catalyzed Buchwald-Hartwig C-N coupling reaction. The reactivity of palladium-catalyzed C-N coupling reaction of the electrically neutral TFB is higher than that of the electron-donating TFA, but less than that of the electron-withdrawing TFT. Thus, unfortunately, the monomers and the corresponding polymers based on TFB with pendant of 8 and TFA with pendant of 3 or 8 were not obtained. The structures and the synthetic routes of the TFT- and TFB-based monomers and the corresponding polymers are outlined in Schemes 1 and 2, respectively.



Scheme 1. Synthetic routes of the monomers based on 2,4,6-trifluoren-2-yltriazine (TFT) (**9a–9d**) and 1,3,5-trifluoren-2-ylbenzene (TFB) (**12a–12c**). Also shown the molecular structures of the monomers based on trifluoren-2-ylamine (TFA) (**13a–13c**). Conditions: i: Pd₂(dba)₃, DPPF, NaO⁶Bu, toluene, reflux; ii: 1) CF₃SO₃H, CHCl₃, 0 °C; 2) 0 °C ~ r.t.; iii: Cul, K₂CO₃, 18-crown-6, *o*-dichlorobenzene, 180 °C; iv: CH₃COCl, anhydrous AlCl₃, CH₂Cl₂; v: SiCl₄, EtOH.



Scheme 2. Synthetic routes of the polymers based on 2,4,6-trifluoren-2-yltriazine (TFT) (P1a–P1d), 1,3,5-trifluoren-2-ylbenzene (TFB) (P2a–P2c), and trifluoren-2-ylamine (TFA) (P3a–P3b). Conditions: Pd(OAc)₂/tricyclohexyl phosphine (P(Cy)₃), toluene, Et₄NOH, deionized water, 90–100 °C.

The polymers were synthesized by palladium-catalyzed Suzuki cross-coupling polycondensation of an equi-molecular mixture of two monomers of TFT derivatives (**9a–9d**) or TFB derivatives (**12a–12c**) or TFA derivatives (**13a–13b**) and **14** to give **P1a–P1d**, **P2a–P2c**, and **P3a–P3b**, respectively. The chemical structures of the polymers were verified by ¹H NMR and elemental analysis.

The developed polymers are soluble in conventional organic solvents, like toluene, chloroform, and tetrahydrofuran (THF). Molecular weights of the polymers were determined by gel permeation chromatography (GPC) utilizing THF as a solvent and polystyrene as a standard. As shown in Table 1, except for **P1c**, M_n of the polymers are from 20.9 to 52.9 kDa with polydispersity index (PDI = M_w/M_n) between 1.16 and 2.16. The C, H, and N contents for the polymers are close to those calculated from the feed compositions.

3.2. Thermal properties

As shown in Table 1, all the polymers exhibit good thermal stability with 5% weight-loss temperatures (T_d) over 400 °C due to the introduction of the bulky TFT, TFB, and TFA building blocks into the main chains, which impart the chains with rigidity and non-coplanarity. With the change of the substituents at the C-7 position of the pendent fluorene of TFT and TFB, relatively high glass transition temperatures (T_g) ranging from 56 to 94 °C, 63–79 °C

Table 1Molecular weights and thermal properties of the polymers.

Polymer	M_n (kDa)	M_w (kDa)	PDI	T_d (°C)	T_g (°C)
P1a	36.3	71.7	1.97	424	79
P1b	52.9	114	2.16	420	82
P1c	4.95	5.67	1.14	427	56
P1d	22.3	33.8	1.51	422	94
P2a	40.1	84.3	2.11	424	66
P2b	32.2	37.2	1.16	405	79
P2c	48.7	103	2.11	429	63
P3a	26.3	43.8	1.67	416	89
P3b	20.9	37.5	1.80	423	90

were achieved, respectively. The pendant of 3,6-di-tert-butyl carbazole (7) endows the polymers higher T_g in comparison to those of the polymers with carbazole (6) pendant due to the bulky tert-butyl groups. For P1d, which possesses more bulky pendant of G2 carbazole dendrimer (**8**), T_g up to 94 °C was achieved, which is 15 °C higher than that of P1a with the smallest carbazole pendant. For **P3a** and **P3b**, T_g up to ~90 °C was achieved, which is much higher than those of P1a-P1b and P2a-P2b with the same side chain, respectively. Considering that the above-mentioned three types of polymers possess the identical pendants, the only difference is the structure of the main chain, exactly, the distinct junction of the side chain to the backbone, i.e. electron-donating amine, electron-withdrawing triazine, and electrically neutral benzene. Wherefore, the different T_g of these polymers could be attributed to the difference in rigidity and polarity of the main chains, and thus the unequal molecular interaction. Owing to the much more flexible alkyl chains of bis(9,9-dioctyl-9H-fluoren-2-yl)amine (3) in P1c and **P2c**, these two polymers exhibit the lowest T_g of 56 and 63 °C, respectively, among all the developed polymers.

3.3. Optical properties

In toluene solution, the polymers **P2a** and **P2b** based on the electrically neutral TFB exhibit one distinct absorption band at about 360 nm, which can be attributed to the π - π * transition of the conjugated polymer backbone (Fig. 1) [24]. Besides, they also exhibit one peak combined with a slight absorption shoulder in the range of 280–320 nm that can be attributed to the pendent carbazolyl. Compared to the absorption bands of **P2a** and **P2b**, bath-ochromic shift of about 10 nm was observed for the absorption bands of **P2c**. In our previous work, it was reported that the absorption bands of the polymers containing TFA as a building block of main chain peak at ~400 nm in toluene solution [18]. Therefore, this bathochromic shift can be attributed to the electron-donating component of TFA that acts as the side chain of **P2c** and expands the π -conjugation system compared with the carbazolyl group. For the films, besides the absorption bands at ~360 nm,

P1a

P1b

P1c

P1d

P2a

P2b

P2c

P3a

P3b

P1a

Fig. 1. Normalized UV-vis absorption (Left) and PL (Right) spectra of the polymers in dilute toluene solutions

P1a

P1b

P1c

P1d

P2a

P2b

P₂c

P3a

P3b

280 320 360 400 440 480 520 560 600 350

Wavelength (nm)

PL (a.u.)

PL (a.u.)

(a.u.)

ᆸ

400 450 500 550 600 650 700

Wavelength (nm)

another intense band was observed at \sim 215 nm (Fig. 2), which can be attributed to the $n-\pi^*$ transitions of fluorene. These absorption bands are absent for the solutions since they are overlapped by the absorption of toluene.

For the polymers based on the electron-withdrawing TFT in toluene solution, the absorption band of the $\pi - \pi^*$ transition of the conjugated polymer backbone situates at 390 nm except for P1c at 360 nm, which shifts to the shorter wavelength for 30 nm may be attributed to the retardation of electronic delocalization caused by the twist between the main chains and the side chains of TFA [25]. Noting that due to the intense ICT interaction formed between the electron-withdrawing segment of TFT and the electron-donating component of 3, a broad and intense absorption band was



Fig. 2. Normalized UV-vis absorption (Left) and PL (Right) spectra of the polymers in thin films

observed in the range of 400-470 nm. A slight absorption band was found in the range of 280–320 nm and can be also ascribed to the $\pi - \pi^*$ transition of the pendent carbazolyl for **P1a** and **P1b**. Since there are more carbazole groups in 8 that acts as the pendant in P1d, the absorption band in the range of 280-320 nm is much more intense than those of P1a and P1b, and it is consistent with the absorption in films. Similarly, besides the absorption bands at 360 and 390 nm. another intense band of 215 nm was also observed with a shoulder at 240 nm (Fig. 2) for the films, which can be attributed to the $n-\pi^*$ transitions of fluorene.

For the polymers based on the electron-donating TFA, P3a and **P3b**, the distinct absorption band of the $\pi - \pi^*$ transition of the conjugated polymer backbone is at about 400 nm in both toluene solution and solid film, and a broad absorption band of the pendent carbazolyl was observed in the range of 300-350 nm (Fig. 1) and 280-320 nm (Fig. 2), in toluene solution and solid film, respectively. Compared with the polymers based on the electronwithdrawing TFT and the electrically neutral TFB, the difference of the distinct absorption band can be ascribed to the disparity of the π -conjugation in the polymer backbone.

Similar bathochromic shifts were also observed for their PL spectra recorded in both toluene solution and thin film. For the toluene solutions of the polymers based on TFB, PL spectra peak at 410 and 449 nm, 410 and 439 nm, 425 and 449 nm for P2a, P2b, and P2c, respectively (Fig. 1). For the films, PL spectra peak at 416 nm with a shoulder at 440 nm for P2a and P2b. In comparison, PL spectrum of P2c peaks at 429 nm with a shoulder at 450 nm due to the electron-donating pendant of TFA that expands the π -conjugation. For the polymers based on the electron-withdrawing TFT in toluene solution, PL spectra peak at ~430 and 460 nm for P1a and P1d, 430 and 450 nm for P1b. In comparison, PL spectrum of P1c shifts to the longer wavelength of 480 nm with a slight PL band at 430 nm, which can be attributed to the emissions according to the ICT interaction formed between the electron-withdrawing main chain and the electron-donating side chain and the polymer backbone, respectively. Different from most of ever reported LEPs whose emission colors were tuned by incorporation of low-energy chromophore and thus energy transfer from the high energy chromophore backbone to the low-energy chromophore unit, emission color of P1c was tuned by the ICT interaction between the electron-withdrawing main chain and the electron-donating side chain although either of them emits blue light. Moreover, the PL band according to the ICT interaction dominates the emission spectrum even in a dilute solution. In contrast, for most of the LEPs achieved by incorporation of low-energy chromophore, the PL bands according to the high energy chromophore backbone generally dominates the emission spectra in a dilute solution due to the incomplete energy transfer. For the films, PL spectra peak at ~436 nm with a shoulder at 460 nm for P2a, P2b, and P1d, respectively. In comparison, PL spectrum of P1c in solid film shifts to the longer wavelength and peaks at 482 nm, and the slight emission band at 430 nm according to the polymer backbone shown in the dilute solution disappeared completely in the solid film. Compared with the PL spectra of the polymers based on the electrically neutral TFB in both toluene solution and thin film, all the PL spectra of the polymers based on the electron-withdrawing TFT shift to the longer wavelength, and it can be explained by the strong electron affinity of TFT component and thus the ICT interaction between the electron-donating pendant and the electronwithdrawing backbone. PL spectra of P3a and P3b also shift to the longer wavelength in comparison to the polymers based on the electrically neutral TFB, P2a and P2b, and the electronwithdrawing TFT, P1a and P1b, in both toluene solution and thin film. As compared with the PL spectra of the polymers in toluene solution, the PL spectra of the polymers in thin film slightly shift to



Abs (a.u.)

Abs (a.u.)

Abs (a.u.)

the longer wavelength (Fig. 2), which can be probably ascribed to the aggregation and dielectric environment of the solid films [26,27]. The PL quantum efficiencies are listed in Table 2. It was found that polymers based on TFT and TFB showed much higher efficiencies than those of polymers based on TFA, indicating that polymers contained TFT and TFB could more effectively restrain the aggregation of the molecular chains relative to the polymers based on TFA.

To gain more insights into the photophysical properties of the polymers based on TFT, TFB and TFA, UV-vis absorption and PL spectra in solvents with varying polarity, such as toluene (dielectric constant Dk = 2.38), dichloromethane (DCM) (Dk = 9.1), and THF (Dk = 7.5) were measured [20]. For **P1** containing electronwithdrawing backbone and electron-donating pendants, their photophysical properties in solution are strongly dependent on the solvent polarity. As depicted in Fig. 3, the absorption profile and maxima of P1a, P1b and P1d are almost consistent in varying solvents, suggesting their solvent polarity independent ground state electronic structures and small dipole moments associated with the ICT transitions [28]. It is worth pointing out that the absorption spectrum of P1c displays a bathochromic shifted peak at 379 nm with an emerging shoulder at 440 nm in THF solution compared with that in DCM and toluene solutions, indicating a guite different chain conformation in THF due to the intense ICT interaction. PL spectra of P1a, P1b and P1d in toluene solution show a well-resolved vibronic structure with two emission peaks. In comparison, only one emission peak with broadened emission spectra and obscure vibronic structure was observed in THF and DCM solutions. In addition, their PL spectra in THF and DCM solutions exhibit obvious spectral red-shifts in emission and broader full width at half-maximum (FWHM) compared with that recorded in toluene solution. Note that those are good solvents for all the polymers and the observed red-shift of the PL spectra occurs in rather dilute solutions ($\sim 1 \times 10^{-5}$ M on the basis of the molecular weight of the polymer repeat unit), suggesting that aggregation (inter-molecular) effects are not responsible for the red-shift. This phenomenon could be interpreted that the more polar excited state resulting from a charge-transfer should be stabilized relative to the less polar ground state in a solvent of greater polarity [29]. This excited state stability should result in a red-shift of the emission spectra of the polymers in more polar solvents. Interestingly, PL spectrum of P1c in DCM solution displays two obvious emission peaks at 417 and 560 nm. The emission peak with higher-energy can be attributed to the emission of the polymer backbone, and the emission peak with lower energy can be attributed to the ICT interaction. Different from the toluene and THF solutions, the emission according to the polymer backbone dominates the PL spectrum, indicating higher stability of the excited state of polymer backbone.

Table 2

Optical energy band gaps (E ^{opt}), PL quantum efficiencies (QE _{PL}) and electrochemi	ca
properties of the polymer films.	

Polymer	$E_g^{\text{opt}a}(eV)$	$E_{\mathrm{ox}}\left(V\right)$	$E_{\rm HOMO}^{\rm b}~({\rm eV})$	$E_{\rm LUMO}^{\rm c}({\rm eV})$	QE _{PL} (%)
P1a	2.91	1.25	-5.77	-2.86	27.8
P1b	2.91	1.27	-5.79	-2.88	23.6
P1c	2.58	1.15	-5.67	-3.09	9.2
P1d	2.88	1.17	-5.69	-2.81	21.5
P2a	3.00	1.20	-5.72	-2.72	33.3
P2b	3.00	1.22	-5.74	-2.74	26.7
P2c	2.98	1.18	-5.70	-2.72	21.0
P3a	2.80	0.95	-5.35	-2.55	2.7
P3b	2.80	1.04	-5.44	-2.64	10.5

^a Estimated with the absorption edges of the solid films.

^b Calculated according to HOMO = $-e(E_{ox} + 4.52)$.

^c Calculated from the HOMO energy level and E_g^{opt} .

PL spectra of the polymers **P2** and **P3** also exhibit solvatochromism nature in different solvents (Figs. S1 and S2). However, the maximum emission wavelengths change slightly in solvents with different polarities to give broader FWHM values and obscure vibronic structure in a polar environment. In comparison to the absorption process, absorption bands of **P2** and **P3** are almost consistent in these solvents, suggesting that absorption involves a Franck–Condon transition from the non-dipolar ground state. This is quite different from the excited state that may be possesses a charge-transfer component, which is stabilized by high dielectric constant solvents and thus red-shifts.

3.4. Electrochemical properties

The electrochemical properties of the polymers were investigated by CV. Under the same experimental condition, the redox potential $(E_{1/2})$ of ferrocene/ferrocenium (Fc/Fc⁺) was measured to be 0.28 V to the Ag/Ag⁺ reference electrode. Note that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to vacuum [30,31]. Thus, HOMO energy levels are calculated according to the following equations: HOMO = $-e(E_{ox} + 4.52)(eV)$, where E_{ox} is the onset oxidation potential vs Ag/Ag⁺ [32]. LUMO energy levels of the polymers are estimated from the HOMO energy levels and the optical energy band gaps (E_g^{opt}) . The optical energy band gaps of the polymers are estimated from the absorption edges of the UVvis spectra of the thin films (Table 2). HOMO energy levels of all the TFB-based polymers are about -5.7 eV. With introducing two tertbutyl groups at the 3- and 6-positions of the carbazole component in P2a. slightly reduced HOMO and LUMO energy levels were achieved for P2b. This phenomenon was also confirmed for the TFA- and TFT-based polymers. The decreased HOMO and LUMO energy levels can be attributed to the *tert*-butyl groups that may break the $\pi-\pi$ stacking of carbazoles and fluorenes. Since the electron-donating ability of **3** is stronger than that of carbazole, HOMO energy levels of the polymers containing pendant 3 is higher-lying in comparison to those of the corresponding polymers with carbazole pendant. Due to the electron-withdrawing TFT segments introduced into the skeleton of the polymers P1, LUMO energy levels of the polymers P1 were reduced to -2.8 eV, which are 0.1 eV lower-lying in comparison to those of the polymers P2 based on the electrically neutral TFB. For P1d, which possesses bulky G2 carbazole dendrimer pendant of 8, its HOMO energy level rises to -5.69 eV, which is 0.1 eV higher-lying relative to that of **P1b.** It is worth noting that LUMO energy level of **P1c** was greatly reduced to -3.09 eV, which could be attributed to the strong electron affinity of TFT component and thus the ICT interaction between the electron-donating pendant 3 and the electronwithdrawing unit TFT, rendering the narrowest optical energy band gap of 2.58 eV. In comparison, for P3a and P3b, owing to the introduction of the electron-donor TFA into the main chain and carbazole as the pendant, HOMO and LUMO energy levels ascend to -5.4 and -2.6 eV, respectively, which are higher-lying than the electrically neutral TFB-based polymers P2a and P2b, and the electron-withdrawing TFT-based polymers P1a and P1b. Furthermore, according to the absorption edges of the solid films, their optical energy band gaps are estimated to be 2.80 eV, which is narrower compared to those of P2a-P2b and P1a-P1b.

3.5. Density functional theory calculations

To get further insights into the molecular orbitals of polymers, density functional theory (DFT) calculations of the polymer units based on pendants of carbazole and **3** were performed using the Gaussian suite of programs (Gaussian 03W). To obtain their HOMO and LUMO energy levels, molecular structure optimization



Fig. 3. Normalized UV-vis absorption (Left) and PL (Right) spectra of P1a-P1d in dilute toluene (\bigcirc), DCM (\bigcirc) and THF (\square) solutions.

(halogen and alkyl chain were omitted) and single-point energy calculations were performed at the B3LYP/6-31G(d) and B3LYP/6-311 + G(d,p) levels, respectively. Besides **9a**, **9c**, **12a**, **12c**, and **13a**, calculation of **13c** was also performed for contradistinction, although

it could not be obtained as above-mentioned. As shown in Fig. 4, HOMOs of the polymer units based on TFT and TFB are mainly located at the pendant of carbazole or **3**. In comparison, their LUMOs reside along the central arylene skeleton of TFT and TFB, respectively. For



Fig. 4. Calculated spatial distributions (DFT, Gaussian 03W) of LUMOs (Top) and HOMOs (Bottom) of the monomers. Halogen and alkyl chain were omitted.

the polymer units based on TFA, both of the HOMOs and LUMOs are delocalized over the whole π -conjugation system since the whole molecule is electron-rich. Note that the difference in the HOMO/ LUMO localization is especially pronounced for 9c, in accordance with the intense electron-accepting behavior of the TFT moiety and stronger electron-donor of **3**. Under the assumption that the long wavelength transitions are predominantly determined by the HOMO-LUMO transition, the excitation leads to an ICT interaction from the electron-donor of **3** to the electron-acceptor of TFT moiety [33]. These calculations verify our initial assumption that the electron-rich 3 acts as an electron-donor and the electron-poor TFT unit as an electron-acceptor in the ICT complex. The calculated HOMO and LUMO levels are demonstrated in Table S1. It can be clearly seen that lower-lying LUMO energy level can be obtained by introducing electron-withdrawing moiety of TFT instead of electrically neutral TFB and electron-donor TFA. Moreover, different energy levels can be obtained by the change of the electron-donating moiety. Although the experimental energy levels are somewhat different from the calculated ones, the same trend was ascertained.

3.6. Electroluminescence

To evaluate their electroluminescence properties, double-layer devices with a configuration of ITO/PEDOT:PSS (40 nm)/EML (70–80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al were fabricated, where the developed polymers were used as an EML and TPBI (2,2',2''-(1,3,5-benzenetriyl)-tris-(1-phenyl-1H-benzimidazole)) was used as an electron-transport and hole-block layer. As shown in Scheme 3, due to the lower-lying LUMO and HOMO energy levels of TPBI, electron-injection from the cathode can be enhanced and carrier recombination can be well confined within the EML.

As shown in Fig. 5(a), current densities of the device based on P1a, the polymer based on the electron-withdrawing TFT and carbazole pendant, are higher than those of the device based on P2a, the polymer based on the same pendant and the electrically neutral TFB. It can be attributed to its relatively lower-lying LUMO energy level that facilitates electron-injection from the electrontransport layer of TPBI. Similar phenomenon was also observed for the devices based on the polymers P1b and P2b with 3,6-ditert-butyl carbazole pendant. Current densities of the device based on P3a, the polymer based on the electron-donating TFA and carbazole pendant, are equal to or even higher than those of the device based on P1a, although its LUMO energy level is 0.3 eV higher-lying that that of P1a. The increased current density can be attributed to the higher-lying HOMO energy level of P3a that facilitates hole-injection from the anode. As shown in Table 3, turnon voltages (V_{on}) for electroluminescence (a luminance of 1 cd m⁻² was detected) of the devices are between 2.9 and 5.6 V, and the



Scheme 3. Energy diagram of the devices with the configuration of ITO/PEDOT:PSS (40 nm)/EML (70–80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al.



Fig. 5. (a) Current density and luminance versus voltage and (b) current efficiency versus current density characteristics of the devices with the configuration of ITO/ PEDOT:PSS (40 nm)/EML (70–80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al. EML: P1a–P1d, P2a–P2c, and P3a–P3b.

device based on **P3a** exhibits the lowest V_{on} due to the highest HOMO energy level that facilitates hole-injection and transport from the anode. The turn-on voltages of the devices based on **P1a**–**P1c** are lower than those of the devices based on **P2a–P2c**, respectively, due to their lower-lying LUMO energy levels are more close to the LUMO energy levels of the electron-transport layer TPBI and thus facilitate electron-injection into the EML.

Current efficiency (CE) versus current density characteristics of the devices are shown as Fig. 5(b). The maximum CE (CE_{max}) of the devices based on **P2a**, **P2b**, and **P2c** are 0.85, 0.44, and 1.34 cd A^{-1} ,

Table 3
Summary of the electroluminescent performance of the devices with the configu-
ration of ITO/PEDOT:PSS (40 nm)/EML (70-80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al.

EML	$V_{\mathrm{on}}^{a}(V)$	$L_{\rm max}$ (cd m ⁻²)	CE_{max} (cd A^{-1})	EQE _{max} (%)	CIE(x, y)
P1a	3.2	138	0.12	0.07	(0.23, 0.28)
P1b	4.3	99	0.08	0.1	(0.22, 0.28)
P1c	3.3	3420	4.10	2.45	(0.24, 0.51)
P1d	4.8	1030	1.26	1.27	(0.16, 0.14)
P2a	5.0	1020	1.50	1.44	(0.21, 0.17)
P2b	5.6	910	0.85	0.63	(0.21, 0.18)
P2c	3.8	2560	1.93	1.26	(0.21, 0.16)
P3a	2.9	2090	2.44	3.00	(0.16, 0.12)
P3b	3.2	1650	1.70	1.53	(0.18, 0.19)

 a Turn-on voltage for electroluminescence (a luminance of 1 cd m^{-2} was detected).

respectively. The relatively low efficiency may be attributed to the low carrier balance achieved in the device since these polymers are comprised of only electron-donors of carbazole, 3,6-di-tert-butyl carbazole, and **3** as the pendants. In comparison, the device based on **P1c** exhibits a maximum CE of 4.10 cd A^{-1} , corresponding to external quantum efficiency (EQE) of 2.45%, which is the highest one among all the devices. Since TFA pendant is a well-known hole transporter and TFT is a well-known electron transporter, the introduction of **3** onto TFT as the pendant of the polymer may facilitate hole and electron-transport into the EML to give an improved current density and reduced driving voltage. In addition, carrier balance can be also improved to give an improved CE. Note that the devices based on P1b, P2b, and P3b show lower CE in comparison to the devices based on P1a, P2a, and P3a, respectively. The decreased efficiency can be attributed to the reduced carrier transport property and thus the carrier balance due to the bulky tert-butyl groups combined with carbazole. It was found that the efficiency of the device based on P1d is much higher than that of P1a and P1b, which can be attributed to more carbazole units in the pendant 8 of P1d to give an improved charge carrier balance and higher CE. Aside from the improved efficiency, the improved hole transport also induces the carrier recombination zone apart from the interface of EML and anode for the device, restraining excimer formation at the interface of EML and anode to give an improved color purity with CIE coordinates of (0.16, 0.14).

EL spectra of the devices based on **P3a** and **P3b** peak at 446 and 448 nm, respectively, with a subsidiary peak at 472 nm (Fig. 6), which is consistent with their PL spectra in solid film state, indicating that both EL and PL emissions mostly arise from the same excited state or



Fig. 6. EL spectra of the devices based on the polymers as an EML with the configuration of ITO/PEDOT:PSS (40 nm)/EML (70–80 nm)/TPBI (30 nm)/CsF (1.5 nm)/Al. EML: P1a–P1d, P2a–P2c, and P3a–P3b.

the same type of excitons [34]. However, a long tail was found in the EL spectra at the wavelengths longer than 500 nm for the devices based on **P2a** and **P2b**, which is absent in the corresponding PL spectra. It is anticipated that the carrier recombination zone in these devices may be close to TPBI because of the disappointing electrontransport capacity of TFB and the long tail found for the devices based on P2a and P2b may be according to the excimer formed at the interface of EML and TPBI. The EL spectra of the devices based on P1a and P1b peak at 464 and 466 nm, respectively, with larger FWHM values compared with the EL spectra of the devices based on P3a-P3b and P2a–P2b. It is suspected that the wide EL spectra may be generated from the carrier recombination zone that is close to PEDOT: PSS because of the relatively good electron-transport capacity of TFT. Similar to the PL spectrum, bathochromic shift was also observed in the EL spectrum for the device based on P1c, and it can be attributed to the strong electron affinity of the electron-acceptor TFT that induces the ICT interaction with the pendant of electron-donor 3. Due to the ICT interaction, the emission colors of the devices based on the TFT-based polymers P1 could be effectively tuned in the region of deep-blue with CIE coordinates of (0.16, 0.14) and light-green with CIE coordinates of (0.24, 0.51) for the polymers based on TFT by introducing various substituents onto the pendent fluorene as the pendants (Table 3). In addition, efficient deep-blue light emission was achieved for the device based on P3a as an EML, that shows a maximum CE of 2.44 cd A^{-1} , corresponding to EQE of 3.00%, with CIE coordinates of (0.16, 0.12). Moreover, the CIE coordinates of the deep-blue device is close to the National Television System Committee (NTSC) and High Definition Television (HDTV) standard blue with CIE coordinates of (0.16, 0.07) and (0.15, 0.06), respectively.

4. Conclusions

In summary, a series of LEPs based on the building blocks of electron-donating TFA (P3a-P3b), electrically neutral TFB (P2a-P2c), and electron-withdrawing TFT (P1a–P1d) were successfully synthesized via palladium-catalyzed Suzuki cross-coupling polycondensation. It was found that the photophysical properties of P1 in solution are strongly dependent on the solvent polarity, and all of the polymers displayed positive solvatochromism nature in the emission spectra in different solvents. Moreover, their emission color could be effectively tuned by changing the structure of the main chain, from the electron-donating TFA to the electrically neutral TFB and the electron-withdrawing TFT. Aside from the main chain, their emission color could also be effectively tuned by changing the substituent at the pendent fluorene of TFT, TFB, and TFA. Deep-blue light emission was achieved for the device based on **P1d** as an EML, giving a maximum CE of 1.26 cd A⁻¹, corresponding to EQE of 1.27%, with CIE coordinates of (0.16, 0.14). Due to the intense ICT interaction, light-green emission was achieved for the device based on **P1c** that shows the highest maximum CE of 4.10 cd A^{-1} , corresponding to EQE of 2.45%, with CIE coordinates of (0.24, 0.51). The current results provide a promising approach to design LEPs by introducing various electron-acceptors and electron-donors as building blocks of main chain or side chain for tuning their emission color as well as energy level.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2012.11.050.

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