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Novel fluorene/trifluoromethylphenylene copolymers: Synthesis, spectra stability and electroluminescence

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ABSTRACT

A group of novel fluorene-based copolymers were synthesized and characterized. The trifluoromethylphenylene unit was introduced into the copolymer backbone and its content ratio was varied from 10 mol% to 50 mol%. The electronic bandgap of the copolymer increases regularly with increasing trifluoromethylphenylene ratio. In contrast to pure polyfluorene, the deep-blue fluorescence of these copolymers is quite stable and not contaminated by the well-known green emission associated with fluorenone defects. The copolymers were used as an emitting layer to fabricate organic light-emitting diodes with a pure blue electroluminescence with a CIE coordinate $y \leq 0.10$ obtained for most copolymers. Whilst the presence of the trifluoromethylphenylene units in the copolymers seemed unfavorable for charge injection and device current, improved spectral purity and stability in both the photoluminescence and electroluminescence were noted and ascribed to the electron-withdrawing nature of the trifluoromethylphenylene units and the enhanced anti-autoxidation ability of the fluorene rings in these copolymers.

1. Introduction

Polyfluorene (**PF**)-type polymers have been established as promising blue light-emitting materials for application in organic light-emitting diodes (OLEDs). They possess many merits such as high fluorescent quantum yields, easy syntheses and structure modification, good solubility in common organic solvents and acceptable charge mobility [1–3]. However, an undesired low-energy “green” band covering a broad spectral range from 500 to 600 nm is frequently generated in both photoluminescence (PL) and electroluminescence (EL) of **PFs** during operation, which not only damages the blue color purity and stability but also limits the emission efficiency [4].

The undesired green emission band has been attributed to either aggregate [5], excimer [6], or keto defects [4b]. After the intensive debate on the true origin of this emission band, it is more acceptable that it stems from the emissive fluorenone defects of **PFs**, which are generated by chemical oxidation of the monoalkylfluorene impurities at the 9-position carbon during polymer preparation or operation in air for a prolonged period [4b,7–9]. Accordingly, polyfluorenes were carefully prepared without monoalkylfluorene defects [10] and some attempts were also taken to remove the generated monoalkylfluorene impurities [11]. Furthermore, various approaches have been exploited to increase the anti-oxidation ability of the 9-position carbon in fluorene moieties and thus to suppress the green emission. One example was to construct a rigid backbone in the fluorene moieties to inhibit the oxidation of the 9-position carbon since the oxidation of the 9-position carbon involves hybrid state conversion from sp^3 to sp^2 and thus the change of bond angles. In this way Park et al. developed a stable blue emitting **PF** derivative with CIE coordinates of (0.17, 0.12) [12]. Another strategy was to decrease the electron density at 9-position of fluorene ring by introducing certain electron-deficient groups in the backbone or sidechains. In our previous report [13], the fluorene copolymers with di(tert-butyl) phenoxysulfonyl side groups showed stable blue PL even after thermal annealing in air and exhibited pure blue EL. The anti-oxidation behavior and improved spectral stability of these **PFs** were suggested to benefit from the strong electron-withdrawing nature of the sulphonate side groups. Similarly, the strong electron-deficient 2,8-dihexyldibenzothiophene-S,S-dioxide-3,7-diyl unit was also used as the building block to synthesize pure blue light-emitting **PF** derivatives. However, the EL efficiency of those polymers was only 0.24 cd A^{-1} with blue color coordinates of (0.18, 0.15) [14].

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With a better understanding of the origin of the green emission in fluorene-based polymers, it is possible to choose more appropriate electron-withdrawing groups to avoid the formation of the keto defects to obtain a pure blue emission. For this purpose, both the substituent type and its content ratio are evidently two important factors to determine the performance of the polyfluorene derivatives. In this paper, we report the synthesis and properties of a series of novel fluorene-based copolymers containing trifluoromethylphenylene comonomer on the backbone (Scheme 1). The trifluoromethylphenylene unit was selected as an important building block with the expectation that the electron-withdrawing nature of trifluoromethyl groups tunes the electron density at the 9-position carbon of fluorene rings through the π-conjugation channels and thus increases the anti-oxidation ability of the polymers [15]. Although a phenylene unit has been used together with fluorene to construct copolymers [16], this is the first report of fluorene-based copolymers containing trifluoromethylphenylene units on the backbone. The content ratio of the trifluoromethylphenylene unit was varied from 10 mol% (**PF-10CF$_3$**) gradually to 50 mol% (**PF-50CF$_3$**). For comparison, poly(9,9-dioctylfluorene) (**PFO**) was also synthesized and studied under the same conditions. The PL spectral stability of these polymers were investigated by monitoring the emission spectra before and after thermal annealing in air. These polymers were also used as the emitting layer in fabricated OLEDs. The results show that, the energy band gaps of these copolymers were regularly tuned with the content ratio of the trifluoromethylphenylene unit and all of these copolymers emit efficient deep-blue fluorescence. Both the PL and the EL spectra of these copolymers were never contaminated by a green emission band, even after the samples were thermally annealed in air for 2 h (for PL). Most copolymers exhibited stable deep-blue EL with CIE coordinate $y \leq 0.10$ in their OLEDs. The luminance and efficiency of these new OLEDs are better than or comparable with those reported polyfluorene derivatives [12,13,14]. Furthermore, the EL performance of these copolymers depends on the ratio of the trifluoromethylphenylene unit, the efficiency decreases with increasing trifluoromethylphenylene ratio.

2. Experimental

2.1. Materials and methods

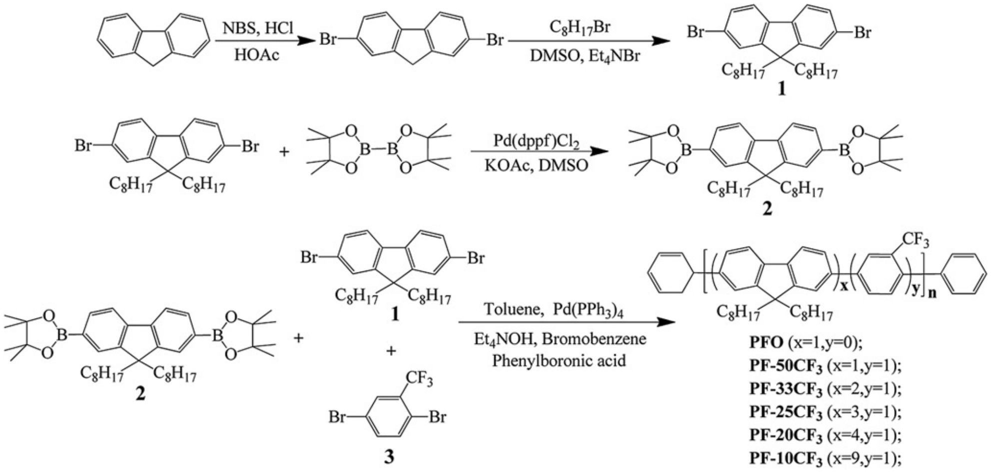
Chemicals, reagents and solvents from commercial sources are of analytical or spectroscopy grade and used as received without further purification. ^{1}H NMR spectra were recorded on a Varian INOVA spectrometer (400 MHz). Number-average (M_n) and weight-average (M_w) molecular weights were determined by GPC method using a viscotek TDA 302 instrument with THF as retention solvent and monodisperse polystyrenes (PS) as standards. Elemental analysis was performed on a Carlo–Eriba 1106 elemental analyzer. The UV–vis absorption and fluorescence spectra measurements were recorded on a Perkin–Elmer Lambda 35 UV–Visible spectraphotometer and a Perkin–Elmer LS55 fluorescence spectrometer, respectively. The fluorescence quantum yields were determined against quinine sulfate as the standard ($\Phi = 0.55$ in 0.1 N H_2SO_4) [17].

2.2. Device fabrication and measurements

The pre-cleaned ITO glass substrates (30 Ω $\square^{-1}$) were treated by UV-Ozone for 20 min. PEDOT/PSS (Bayer AG) was spin-coated on pre-treated ITO substrates from aqueous dispersion and baked at 120 °C for 1 h. Subsequently the polymer solutions (12 mg mL^{-1} in chlorobenzene) were filtered through 0.45 μm PTFE filter and spin-coated on PEDOT/PSS film. The thickness of polymer films was controlled to 40 nm by adjusting the spin rate. The substrate was transferred into a vacuum chamber to deposit the TPBI layer with a base pressure less than 10^{-6} torr. Finally, the device fabrication was completed by thermal deposition of LiF (10 nm) and then capping with Al (100 nm) cathode. The emitting area of each pixel is determined by overlapping of the two electrodes(9 mm^2). The EL spectra, CIE coordinates, and current-voltage-luminance relationships of devices were measured with computer-controlled Spectrascan PR 705 photometer and a Keithley 236 source-measure-unit. All the measurements were carried out at room temperature.

2.3. Synthesis of polymers

The monomers **1** and **2** were synthesized according to the literature methods [18], **3** was purchased from Alfa Aesar and used without further purification. The following general procedure was used for the preparation of all the polymers. To a 50 mL two-necked flask was added the appropriate diboronate (1 equiv), the appropriate dibromide (1 equiv), Pd(PPh$_3$)$_4$ (0.005 equiv) and toluene (15 mL). The flask equipped with a condenser was then evacuated and filled with argon for three times to remove traces of air. The mixture was stirred at 85 °C for 5 min before an aqueous tetraethylammonium hydroxide solution (20%, 4.3 equiv) was added. The



Scheme 1. Synthetic routes of polymers.

mixture was then stirred for 24 h at 85 °C under nitrogen. Bromobenzene (1 equiv) was added to the mixture and stirred for 12 h. Phenylboronic acid (1 equiv) was added to the mixture after which the mixture was stirred for 12 h. The mixture was cooled to room temperature and dropped by pipette into a stirred solution of methanol (100 mL) in a beaker. The precipitate was isolated and extracted for 12 h in a Soxlet apparatus with acetone, the resulting polymers were collected and dried under reduced pressure.

PFO: Light yellow powder (yield: 81.5%). GPC (THF, PS standard): $M_n = 202{,}215\ \text{g mol}^{-1}$, $M_w = 269{,}000\ \text{g mol}^{-1}$, PDI = 1.33; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.84–7.32 (m, ArH), 2.12 (br, CH_2), 1.25–1.15 (m, CH_2), 0.84–0.80 (m, CH_2+CH_3);

PF-50CF$_3$: White fibrous solid (yield: 93.0%). GPC (THF, PS standard): $M_n = 22{,}360\ \text{g mol}^{-1}$, $M_w = 35{,}944\ \text{g mol}^{-1}$, PDI = 1.67; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.08 (s, ArH), 7.89–7.40 (m, ArH), 2.12 (br, CH_2), 1.23–1.12 (m, CH_2), 0.86–0.78 (m, CH_2+CH_3); Elemental analysis found: C 79.30, H 8.00.

PF-33CF$_3$: White powder (yield: 83.3%). GPC (THF, PS standard): $M_n = 10{,}573\ \text{g mol}^{-1}$, $M_w = 12{,}065\ \text{g mol}^{-1}$, PDI = 1.14; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.08 (s, ArH), 7.91–7.40 (m, ArH), 2.12 (br, CH_2), 1.14 (m, CH_2), 0.86–0.80 (m, CH_2+CH_3); Elemental analysis found: C 82.69, H 8.96.

PF-25CF$_3$: White powder (yield: 86.3%). GPC (THF, PS standard): $M_n = 12{,}162\ \text{g mol}^{-1}$, $M_w = 14{,}392\ \text{g mol}^{-1}$, PDI = 1.18; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.08 (s, ArH), 7.89–7.41 (m, ArH), 2.12 (br, CH_2), 1.14 (m, CH_2), 0.83–0.80 (m, CH_2+CH_3); Elemental analysis found: C 85.57, H 9.58.

PF-20CF$_3$: Light yellow powder (yield: 90.3%). GPC (THF, PS standard): $M_n = 10{,}508\ \text{g mol}^{-1}$, $M_w = 11{,}645\ \text{g mol}^{-1}$, PDI = 1.11; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.08 (s, ArH), 7.90–7.41 (m, ArH), 2.12 (br, CH_2), 1.20–1.14 (m, CH_2), 0.83–0.80 (m, CH_2+CH_3); Elemental analysis found: C 86.28, H 9.94.

PF-10CF$_3$: Light yellow powder (yield: 92.3%). GPC (THF, PS standard): $M_n = 9020\ \text{g mol}^{-1}$, $M_w = 10{,}606\ \text{g mol}^{-1}$, PDI = 1.17; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.08 (s, ArH), 7.89–7.41 (m, ArH), 2.12 (br, CH_2), 1.25–1.14 (m, CH_2), 0.83–0.80 (m, CH_2+CH_3); Elemental analysis found: C 87.33, H 10.09.

3. Results and discussion

3.1. Synthesis

The general synthetic routes used to access these fluorene-based copolymers and the reference polymer **PFO** are outlined in Scheme 1. The key step was a Suzuki polycoupling reaction of monomer **2** (1 equiv), with **1** and **3** (totally 1 equiv) in the appropriate molar ratios ([3] = 0, **PFO**; [1] = 0, **PF-50CF$_3$**; [**1**]/[**3**] = 0.5, **PF-33CF$_3$**; [**1**]/[**3**] = 1, **PF-25CF$_3$**; [**1**]/[**3**] = 1.5, **PF-20CF$_3$**; [**1**]/[**3**] = 4, **PF-10CF$_3$**). The reaction was performed in toluene solution with [Pd(PPh_3)$_4$] (0.005 equiv) as catalyst and aqueous tetraethylammonium hydroxide (4.3 equiv.) as an emulsifying base. The polymers were end-capped with phenyl groups by adding bromobenzene and phenylboronic acid successively upon cessation of the polymerization. Monomers **1** and **2** were synthesized according to literature methods as shown in Scheme 1 [18]. The copolymers were obtained in high yield typically over 80% and have good solubility in common organic solvents such as tetrahydrofuran, dichloromethane and toluene. The number average molecular weights (M_n) of these copolymers were determined by gel-permeation chromatography (GPC) using polystyrene (PS) standard and ranged from 22,360 to 9020. The corresponding polydispersity indexes (PDI, PDI = M_w/M_n) were from 1.67 to 1.11 for the new polymers. The actual ratio of 9,9-dioctylfluorene (DOF) to trifluoromethylphenylene (TFMP) in the copolymers was calculated from elemental analysis. The details of the calculation method are shown in the Supporting information. A brief summary of these parameters is listed in Table 1.

3.2. Photophysical properties

The photophysical properties of these polymers were investigated by means of electronic absorption and photoluminescence (PL) spectra in dilute dichloromethane solutions and solid films on quartz plates. As shown in Fig. 1a, all the copolymers exhibit structureless absorption with the peaks located from 345 to 381 nm, which are ascribed to the $\pi-\pi^*$ transition of the polymer backbone. With gradually increasing the ratio of the trifluoromethylphenylene unit from zero (**PFO**) to 50 mol% in **PF-50CF$_3$**, the absorption spectrum reveals a general trend of a blue shift. This indicates that the introduction of trifluoromethylphenylene units reduces the π-electron conjugation extent along the polymer backbone mainly due to the less coplanarity of the adjacent fluorene and trifluoromethylphenylene rings in comparison with the two fluorene rings in PFO, thus resulting in a blue shift of absorption peaks and the increase of the highest occupied molecular orbital (HOMO)-the lowest unoccupied molecular orbital (LUMO) energy gap of the individual molecules [19]. Upon photoexcitation at the absorption maximum, all these polymers emit strong deep-blue fluorescence. As shown in Fig. 1b, the fluorescence spectra of these polymers show three well-resolved vibronic bands. For example, the three bands for **PF-25CF$_3$** are located at 415, 437, and 471 nm, and those for **PFO** are at 417, 440, and 475 nm. The three fluorescence bands of each polymer can be ascribed to the electronic transitions from the lowest vibronic level of the ground state ($S_{0,0}$) to different vibronic levels of the first singlet excited state ($S_{1,0}$, $S_{1,1}$, and $S_{1,2}$). In consistence with the absorption spectra, a blue shift is also observed in the PL spectra of these polymers when increasing the ratio of trifluoromethylphenylene units. A blue shift of 19 nm was detected for the emission peak from **PFO** to **PF-50CF$_3$**.

From the wavelength difference between the absorption maximum and fluorescence maximum, the Stokes shifts of these

Table 1
Structural characterization, thermal and photophysical data of the polymers.

Polymer	Yield (%)	M_n	M_w/M_n	DOF/TFMP in feed	DOF/TFMP in polymer[c]	λ_{max}^{abs} (nm)[b]	λ_{max}^{em} (nm)[b]	Φ (%)[a]
PFO	81.5	202,215	1.33	/	/	387/384	417/432	0.63
PF-50CF$_3$	93	22,360	1.67	50/50	44/56	345/345	398/404	0.73
PF-33CF$_3$	83.3	10,573	1.14	67/33	58/42	361/361	413/420	0.72
PF-25CF$_3$	86.3	12,162	1.18	75/25	72/28	370/371	414/422	0.63
PF-20CF$_3$	90.3	10,508	1.11	80/20	77/23	376/377	415/424	0.67
PF-10CF$_3$	92.3	9020	1.17	90/10	84/16	381/382	416/424	0.71

[a] Measured in CH_2Cl_2 solutions with quinine sulfate as the standard ($\Phi = 0.55$ in 0.1 N H_2SO_4).
[b] The data before the slash are for dilute dicholoromethane solutions, and the data after the slash are for solid films.
[c] Calculation method of DOF/TFMP is shown in Supporting Information.

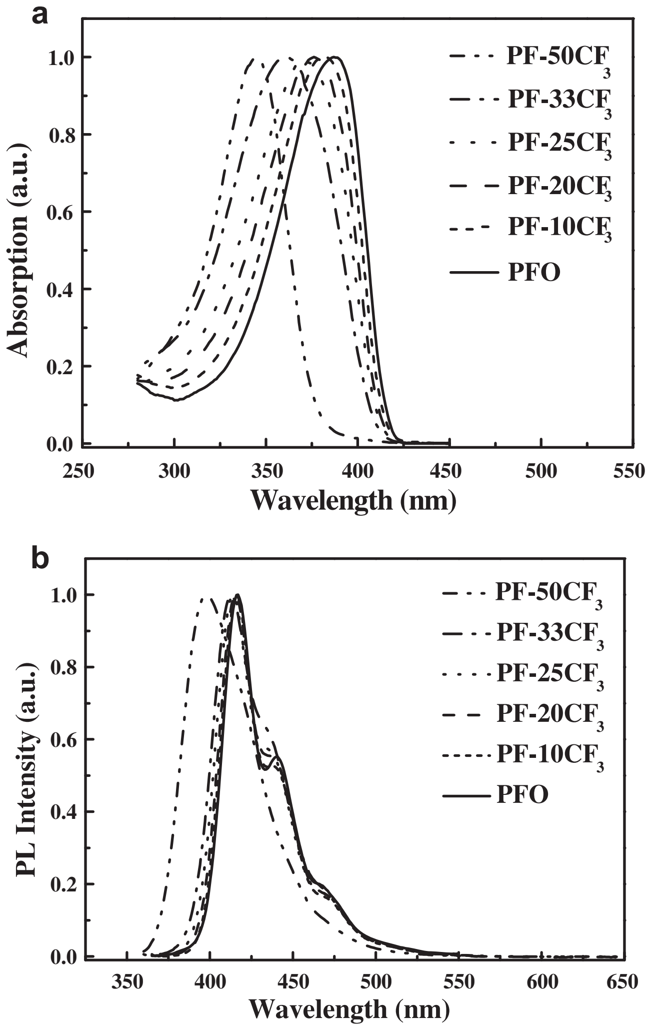


Fig. 1. Absorption (a) and fluorescence (b) spectra of polymers in dilute dichloromethane solutions.

copolymers were determined in the range of 35 nm–53 nm, which are lightly larger than that of **PFO** (30 nm). A larger Stokes shift is usually desired for a light-emitting material since it means a weaker self-absorption and more efficient light output in OLEDs. The fluorescence quantum yields of these copolymers were measured in dilute dichloromethane solutions using quinine sulfate ($\Phi = 0.55$ in 0.1 N H_2SO_4) as a reference [17]. These copolymers showed high PL quantum yields ($\Phi = 0.63–0.73$), most of which are either comparable with or slightly higher than that of **PFO** ($\Phi = 0.63$). The high fluorescence quantum yields of the present copolymers indicate that they may be promising blue light-emitting materials for application in OLEDs.

3.3. Spectral stability

In order to evaluate the spectral stability of the copolymers, copolymer films were made by spin-coating chlorobenzene solutions onto quartz plates and then thermal annealing in air at various temperatures for 2 h. After the films were cooled to the ambient temperature, PL spectra were measured. **PFO** films were also treated and tested under same conditions for comparison. Fig. 2 shows the fluorescence spectra of **PF-33CF$_3$** as an example and **PFO** films before and after annealing. The PL spectra of other analogs before and after annealing are provided in Fig. S1 in the supporting information. It is obvious that the PL spectra of copolymers after thermal annealing are almost identical to those before treatment except for the discernable spectral position change that is probably due to physical change, either instability of measuring environment or aggregation effect in thin films upon thermal treatment [13,20]. The absence of any new emission band in the copolymer films excludes the formation of any new emissive species, even after annealing at such a high temperature of 150 °C for 2 h. However, under the same conditions, the **PFO** film exhibited the well-established green emission band from 500 to 600 nm after annealing at and over 100 °C. Furthermore, the intensity of the green band became higher with increasing temperature. It is obvious that the introduction of the trifluoromethylphenylene units to the copolymer main chain prevented the formation of the green emission band and improved the color purity and stability of their blue fluorescence.

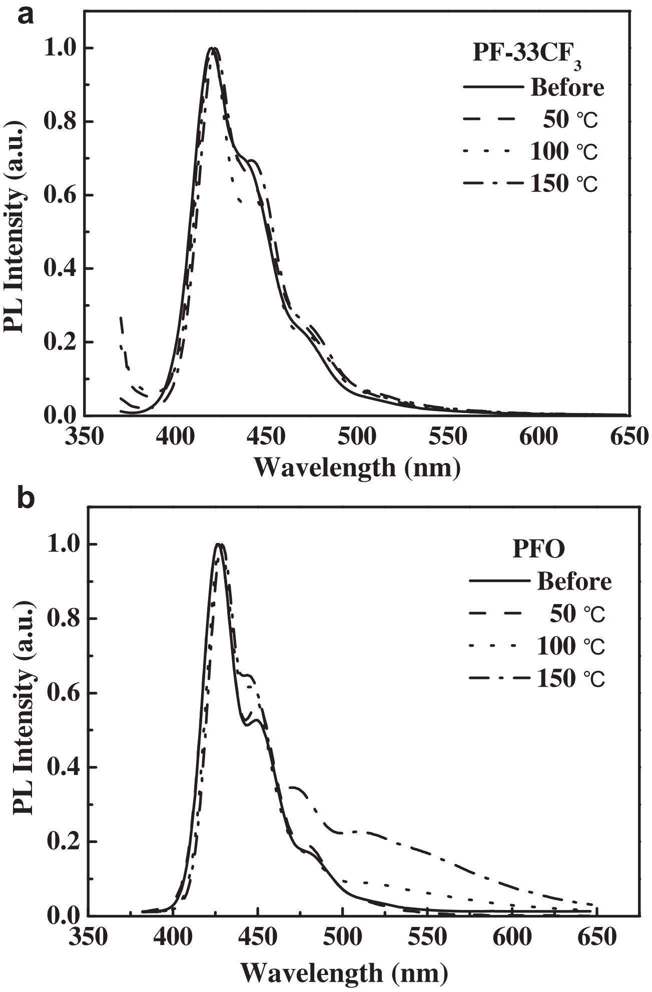


Fig. 2. Fluorescence spectra of (a) **PF-33CF$_3$** and (b) **PFO** films before and after thermal annealing in air at various temperatures.

3.4. Electroluminescence properties of OLEDs

Based on their pure blue fluorescence and relatively high quantum yields, the copolymers were used as the emitting layer to fabricate OLEDs with a configuration of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/polymers (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (200 nm). The fresh **PFO** sample was also used to fabricate OLEDs

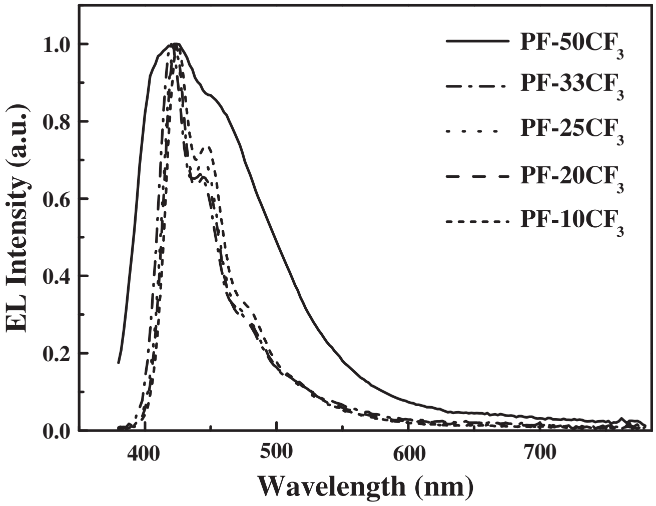


Fig. 3. EL spectra for the copolymers based OLEDs.

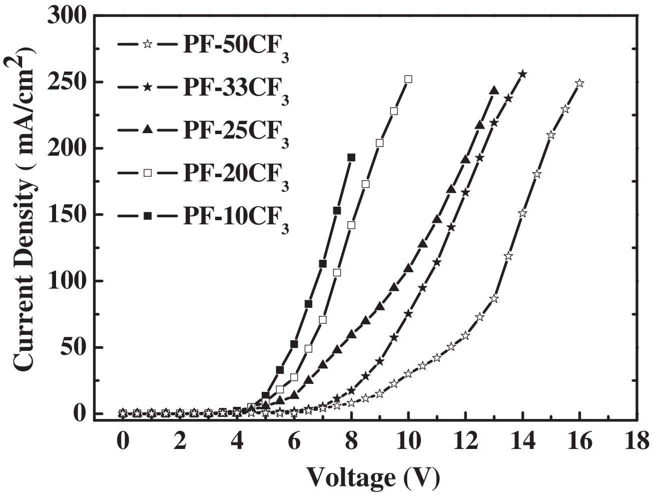


Fig. 4. The current density-voltage characteristics for the polymers based OLEDs.

and investigated for comparison. In these devices, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)) acts as hole injection layer (HIL), TPBI (1,3,5-tris(phenyl-2-benzimidazoyl) benzene) as the electron-transporting (ETL) and hole-blocking layer (HBL). The chemical structures of PEDOT:PSS and TPBI are shown in Fig. S2 in the supporting information. The copolymer based devices emitted bright deep-blue light with emission peaks at around 422 nm, as shown by the EL spectra in Fig. 3. The EL spectra of copolymers are similar to the PL of films with almost identical spectral profiles and peak wavelengths. For copolymers with CF_3 ratio $\leq$ 33%, the full width at half maximum of their EL spectra are only 46, 43, 44, and 45 nm for **PF-10CF$_3$**, **PF-20CF$_3$**, **PF-25CF$_3$**, and **PF-33CF$_3$**, respectively. As shown by the data in Table 2, the copolymers with CF_3 ratio $\leq$ 33% exhibited excellent CIE coordinate $y \leq 0.1$, which is quite close to the pure blue color coordinate y value of 0.08. Moreover, the EL spectra and the CIE coordinates of the copolymers are insensitive to the driving voltage, indicating a stable blue emission. It should be noted that the EL spectrum of **PF-50CF$_3$** device is broader, especially in the long-wavelength region, than its PL spectrum and the EL of other analogs, resulting in the CIE coordinates of (0.176,0.142). It is evident that the EL spectra of all these copolymers with trifluoromethylphenylene units in the backbones are not contaminated by a green emission band even at high driving voltages. However, the EL spectra of the **PFO** device (Fig. S3 in the supporting information) always consists of the blue parts at 438, 466 and 494 nm, which correspond to the fine-structured bands in PL of the fresh **PFO** films, and a broad green component with a peak at 520 nm, even at a low driving voltage of 5 V. The intensity of the green emission band increased with the driving voltage. It should be noted that the two long-wavelength blue bands also ascended along with the green band. The green emission could be observed in EL of the fresh **PFO** device, but not in PL of the fresh PF films. There have been similar reports that the green emission from the fluorenone is stronger in EL than in PL [9,21]. This is because the low-energy keto defects can be excited not only by energy transfer from the fluorene moieties but also by direct charge trapping in the EL device made of **PFO**, while only by energy transfer in PL of **PFO** films. Evidently the presence of these trifluoromethylphenylene units in these copolymers also guaranteed the deep-blue color purity and stability of their EL, which is usually more sensitive to the purity of light-emitting material than PL. It is suggested that the improved spectral purity and stability observed in both PL and EL of these blue light-emitting copolymers benefit from the presence of trifluoromethylphenylene units which take away electron density from the 9-position carbon through π-conjugation channels due to its appropriate electron-withdrawing nature. There have been similar reports to enhance the anti-autoxidation ability and consequent the spectral stability of fluorene-based polymers by incorporating electron-deficient groups in either the main chain or side chain [13,22].

Table 2
EL performance of the polymers based OLEDs.

Polymer	V_{on} (V)[a]	L (cd m^{-2})[b]	η_{ext} (%)[b]	λ_{max} (nm)	CIE (x, y)
PFO	4.8	452 (14 V)	0.53 (6 V)	438	0.179,0.210
PF-50CF$_3$	10	155 (16 V)	0.082 (14 V)	422	0.176,0.142
PF-33CF$_3$	6.2	200 (14 V)	0.11 (8 V)	420	0.168,0.090
PF-25CF$_3$	5	167 (13 V)	0.13 (6 V)	422	0.166,0.098
PF-20CF$_3$	4.1	158 (10 V)	0.15 (5 V)	424	0.168,0.102
PF-10CF$_3$	3.8	130 (8 V)	0.24 (4.5 V)	424	0.164,0.106

[a] Turn-on voltage, recorded at 1 cd m^{-2}.
[b] Maximum values of the devices. The data in the parentheses are the voltages at which the data are recorded.

The current density-voltage (J–V) characteristics of these copolymers based OLEDs are illustrated in Fig. 4. The **PF-10CF$_3$** device has a low turn-on voltage (to deliver a brightness of 1 cd m^{-2}) of 3.8 V, the turn-on voltage increased gradually to 6.2 V for the **PF-33CF$_3$** containing device, and further increased to 10 V for **PF-50CF$_3$**. The J-V curves of these OLEDs exhibited a regular variation in spite of the identical device configuration. With gradual increase of the content ratio of trifluoromethylphenylene units in the copolymer, the turn-on voltage increased gradually and the current density at a given voltage of the corresponding OLED decreased accordingly, which implies a charge injection limited behavior for the copolymer based OLEDs. This is probably because the highest occupied molecular orbital (HOMO) shifts to a lower level with introduction of the trifluoromethylphenylene units in the copolymer backbone and thus the hole injection barrier at PEDOT:PSS/copolymer interface is increased and the higher the content ratio of the trifluoromethylphenylene units, the lower the HOMO level of the corresponding copolymer. As a result, the turn-on voltage is regularly increased with the trifluoromethylphenylene units. The copolymer devices exhibited maximum luminance ranging from 130 to 200 cd m^{-2}, and forward viewing external quantum efficiency from 0.08% to 0.24%, which are comparable with or better than the data for some polyfluorene derivatives reported in the literature [12–14]. In comparison with other analogs, the worse performance for the **PF-50CF$_3$** device, including the broader EL spectra, the lower maximum brightness even at higher voltage, and the lower efficiency, is most likely caused by the less efficient charge injection and the consequent unbalanced charges in the emitting layer. The EL performance data for all these copolymers and **PFO** are summarized in Table 2. Although the luminance and efficiencies of the copolymer devices are lower than those of **PFO**, the copolymers are advantageous in possessing better color coordinates that are more close to those (0.14, 0.08) of the standard blue color. The present work provides an effective strategy to obtain stable deep-blue emitting fluorene-based copolymers by introducing suitable electron-deficient groups in the polymer backbone.

4. Conclusions

In conclusion, a group of fluorene-based copolymers containing various ratios of trifluoromethylphenylene units in the backbone were synthesized and characterized as deep-blue light-emitting materials. In comparison with pure polyfluorene, the introduction of trifluoromethylphenylene units in these copolymers not only increased the fluorescence quantum yields, but also improved the spectral purity and stability of the blue fluorescence. The well-established green emission band at 520 nm from fluorenone defects was never detected for these copolymers even when they were thermal annealed in air at 150 °C. The EL devices fabricated by these copolymers exhibit stable deep-blue emission with CIE coordinate $y \leq 0.10$. The adequate electron-withdrawing nature of the trifluoromethylphenylene units is suggested to be, at least partially, responsible for the enhanced anti-autoxidation ability and improved spectral purity and stability for these copolymers. The present study provides a promising molecular design strategy to tune the anti-autoxidation ability and consequent spectral purity of light-emitting materials by incorporating electron-deficient groups such as trifluoromethylphenylene.

Acknowledgments

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.01.019.

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