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Pendant-decorated polytriphenylamine derivative: potential blue-emitting and hole-transporting material

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Abstract Using Suzuki coupling reaction, we successfully synthesized a conjugated polymer with alternating fluorene and triphenylamine as the main chain and bearing bulky (2,3,4,5-tetraphenyl) phenyl pendants: poly(9,9-dioctyl)-2,7-fluorene-*co*-*N*-4-(2,3,4,5-tetraphenyl)diphenyl-4,4′-diphenylamine (PFT-TPP). This polymer is readily soluble in common organic solvents, has good thermal stability, and readily forms thin film by solution processing. It has an optical bandgap of ca. 2.90 eV, as indicated by the UV–vis investigation. The PL emission of PFT-TPP peaks at 447 nm in dilute THF solution and at 444 nm in a solid film. PFT-TPP shows relatively high HOMO (−5.30 eV) and LUMO levels (−2.40 eV) by cyclic voltammetry, due to the high content of electron-donating triphenylamine segments in the polymer backbone.

Keywords Triphenylamine · Fluorene · Pendant · Blue-emitting · Hole-transport

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Introduction

Over the past 15 years, there has been an increased interest in the preparation of triarylamine derivatives due to their many uses in the optoelectronics field, in areas such as organic light-emitting diodes (OLEDs) [1–5], field-effect transistors [6], photovoltaic devices [7, 8], nonlinear optics [9–11], and electrochromic materials [12, 13]. The most attractive application of triarylamines is their use as hole-transport materials (HTMs) in OLEDs [14–20], because triarylamines have low ionization potential, good electrochemical stability and high hole mobility. In addition, in many cases, triarylamines also show relatively high LUMO (the lowest unoccupied molecular orbital) levels, which endow them with good electron-blocking capability [21, 22].

However, despite their excellent electronic characteristics, the applications of many small molecular triarylamines are limited due to their unsatisfactory thermal and morphological stability [23]. To overcome these limitations, two strategies are frequently adopted. The first is to prepare bulky pendant-substituted, starburst-shaped triarylamines, which effectively increases the glass-transition temperature (T_g) and morphological stability [24, 25]. The second strategy is to incorporate the triarylamines into polymers, either as backbones or as pendants to the main chains [17, 26]. With these modifications, the relatively inexpensive and simpler techniques for device fabrication, e.g., spin-coating and inkjet-printing, can be used.

Triarylamine- and fluorene-based materials are currently of particular interest because of their potential in realization of high efficiency blue light emitting diodes [1–3, 27, 28]. The introduction of triarylamines has substantially improved their electroluminescent performance while also lowering the operation voltage [1–3, 27, 28]. As well, impressive time-of-flight (TOF) hole mobility (on the order of 3×10^{-4} to 3×10^{-3} $\mathrm{cm^2\ V^{-1}\ S^{-1}}$) [29] has been realized in a series of conjugated polymers consisting of alternating triarylamine and fluorene. In these polymers, the fluorene segments function as more than just chemical linkers; they also significantly contribute to the overall hole mobility [29].

In this study, we describe a simple synthesis procedure for preparation of a bulky pendant-decorated triphenylamine derivative: *N*,*N*-bis(4-bromophenyl)-4′-[(2,3,4,5-tetraphenyl)phenyl]phenylamine (monomer **5**). The presence of dibromine sites in this monomer offers synthetic flexibility for the further modification of its chemical structure, which now allows for the preparation of small molecular hole-transporting/emitting materials with modified thermal and morphological stability. From this monomer, we have prepared a conjugated polymer composed of alternating fluorene and pendant-substituted triphenylamine: poly(9,9-dioctyl)-2,7-fluorene-*co*-*N*-4-(2,3,4,5-tetraphenyl)diphenyl-4,4′-diphenylamine (PFT-TPP), via Suzuki coupling reaction. Some basic characterizations, such as the UV–vis absorption, the PL emission, and the electrochemical properties of this polymer, are described in the current study. This polymer shows good potential as a candidate for use as a blue-emitting and hole-transporting material for OLEDs.

Experimental part

Materials

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and were used as received. Triethylamine (NEt_3), tetrahydrofuran (THF) and toluene were distilled from sodium at the presence of benzophenone and degassed before use. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was prepared according to the published procedure and has been described elsewhere [30].

Instrumentation

The ^{1}H NMR and ^{13}C NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating, respectively at 400 MHz (for ^{1}H) and 100 MHz (for ^{13}C) in deuterated chloroform solution with tetramethylsilane as reference. IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elemental Co.). Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV–visible absorption spectra were recorded on a SHIMADZU UV-2450 UV–vis spectrophotometer. PL spectra were recorded on HITACHIF-4500 spectrophotometer. Cyclic voltammetry was carried out on a CHI660C electrochemical workstation with platinum electrodes at scan rate of 50 mV s^{-1} against a saturated calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). Thermogravimetric analysis (TGA) was conducted on a NETZSCH STA 449 °C at a heating rate of 20 °C min^{-1} in air.

Synthesis of monomers

*Synthesis of N,N-bis(4-bromophenyl)aniline (**1**)*

Toluene (110 mL), aniline (10.22 g, 109.7 mmol), 1-bromo-4-iodobenzene (69.8 g, 246.7 mmol), phenanthroline (0.74 g, 4.0 mmol), cuprous chloride (CuCl) (0.43 g, 4.0 mmol), and potassium hydroxide (KOH) (flakes, 86%, 58.9 g, 861.4 mmol) were added sequentially to a 500 ml three-necked flask equipped with condenser, mechanical stirrer, nitrogen inlet and outlet under nitrogen. The reaction mixture was heated to reflux in 30 min and was stirred at refluxing for 48 h. Then the mixture was cooled to 75 °C, and 150 ml of toluene and 100 ml of distilled water were used to extraction. The toluene phase was separated, dried with anhydrous magnesium sulfate ($MgSO_4$), filtered and vacuum distilled. The crude product was purified by silica column chromatography using petroleum ether as eluent to give **1** (26.0 g, 60%) as colorless viscous liquid. FT-IR (KBr, cm^{-1}): 3083, 3062, 3034, 1580, 1484, 1453, 1327, 1310, 1274 (C–N), 1172, 1104, 895, 826, 753, 706, 666. ^{1}H NMR

(400 MHz, $CDCl_3$). δ (ppm): 7.36–7.34 (d, 4H), 7.30–7.26 (t, 2H), 7.09–7.07 (m, 3H), 6.96–6.94 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 146.86, 146.49, 132.30, 129.51, 125.37, 124.56, 123.70, 115.40. GC–MS: $m/z = 403$.

*Synthesis of N,N-bis(4-bromophenyl)-4′-iodophenylamine (**2**)*

N,N-bis(4-bromophenyl)aniline (**1**) (2.02 g, 5.0 mmol), potassium iodide (0.83 g, 5.2 mmol), potassium iodate (1.6 g, 7.7 mmol), and acetic acid (15 mL) were added sequentially to a 50 mL of two-necked round bottom flask equipped with condenser, magnetic stirrer, nitrogen inlet and outlet under nitrogen. The reaction mixture was stirred overnight at 80 °C under nitrogen. Then the mixture was cooled to room temperature and poured into 200 mL of water. The precipitate was collected and redissolved by CH_2Cl_2, washed with aqueous $Na_2S_2O_3$ and dried over anhydrous $MgSO_4$. After removing the solvent, the residue was recrystallized from acetone to afford the target product as white solid. Yield: 1.54 g (61%). FT-IR (KBr, cm^{-1}): 3053, 1573, 1485, 1312, 1282, 1270 (C–N), 1173, 1103, 1071, 1003, 939, 818, 709, 666. ^{1}H NMR (400 MHz, $CDCl_3$). δ (ppm): 7.58–7.52 (d, 2H), 7.41–7.32 (d, 4H), 6.99–6.89 (d, 4H), 6.84–6.77 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 146.80, 145.98, 138.48, 132.59, 125.84, 125.79, 116.23, 86.40 (C–I). GC–MS: $m/z = 529$.

*Synthesis of N,N-bis(4-bromophenyl)-4′- (trimethylsilylethynyl) phenylamine (**3**)*

To a 50 mL of two-necked round bottom flask containing $Pd(PPh_3)_2Cl_2$ (65.8 mg, 0.094 mmol), CuI (18.9 mg, 0.189 mmol), and *N,N*-bis(4-bromophenyl)-4′-iodophenylamine (**2**) (1.0 g, 1.89 mmol) in NEt_3 (5.5 mL) and THF (11 mL) was added trimethylsilylacetylene (0.196 g, 2.0 mmol) under N_2. The reaction mixture was stirred at room temperature for 24 h. After that it was filtered and the solvent was removed in vacuo. Silica gel column chromatography (petroleum ether as eluent) gives the final product as colorless viscous liquid (0.69 g, 73%). FT-IR (KBr, cm^{-1}): 3037, 2958 ($-CH_3$), 2155 ($C \equiv C$), 1604, 1583, 1504, 1485, 1314, 1286, 1270 (C–N), 1249, 1072, 1009, 861, 760, 709, 649. ^{1}H NMR (400 MHz, $CDCl_3$). δ (ppm): 7.39–7.30 (dd, 6H), 6.96–6.90 (dd, 6H), 0.25–0.21 (s, 9H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 147.06, 145.92, 133.21, 132.56, 126.10, 122.91, 117.35, 116.36, 104.88 ($Ar-C' \equiv C$), 93.85 ($C \equiv C'-Si$), 0.05 ($Si-CH_3$).

*Synthesis of N,N-bis(4-bromophenyl)-4′-ethynyl-phenylamine (**4**)*

To a solution of *N,N*-bis(4-bromophenyl)-4′-(trimethylsilylethynyl) phenylamine (**3**) (0.6 g, 1.2 mmol) in a mixture of THF (20 mL) and methanol (10 mL) was added 0.4 mL of KOH solution (aq., 20%). The reaction mixture was stirred for 1 h at room temperature, and the solvent was removed in vacuo. The residue was recrystallized from ethanol to afford the target compound as pale-yellow solid (0.461 g, 90%). FT-IR (KBr, cm^{-1}): 3297 ($C \equiv C-H$), 3059, 3036, 2104 ($C \equiv C$), 1605, 1581, 1505, 1484, 1314, 1275, 1175, 1104, 1072, 1007, 830,727. ^{1}H NMR (400 MHz, $CDCl_3$). δ (ppm): 7.38–7.34 (dd, 6H), 6.97–6.94 (dd, 6H), 3.04 (s, 1H, C $\equiv$ C–H). ^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 147.34, 145.86, 133.34, 132.59, 126.17, 122.81, 116.47, 116.15 (Ar–C′ $\equiv$ C), 83.48 (C $\equiv$ C′–H).

Synthesis of N,N-bis(4-bromophenyl)-4′-[(2,3,4,5-tetraphenyl)phenyl]phenylamine (5)

N,*N*-bis(4-bromophenyl)-4′-ethynyl-phenylamine (**4**) (0.256 g, 0.6 mmol) was refluxed with tetraphenylcyclopentadienone (0.282 g, 0.72 mmol) in 15 mL of *o*-xylene under nitrogen atmosphere for 6 h. After that the reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The crude product was column chromatographied (silica, petroleum ether: CH_2Cl_2 = 2:1, v/v) to afford the target compound as white solid (0.456 g, 96%). FT-IR (KBr, cm^{-1}): 3052, 3021, 1598, 1574, 1509, 1484, 1310, 1266, 1069, 1006, 815, 761, 695, 650. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58–7.56 (s, 1H), 7.34–7.28 (d, 4H), 7.22–7.14 (m, 5H), 7.05–6.99 (d, 2H), 6.99–6.76 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.37, 144.96, 141.70, 141.67, 140.79, 140.24, 140.20, 140.05, 139.90, 139.35, 139.27, 137.19, 132.25, 131.58, 131.52, 131.44, 131.05, 130.89, 129.95, 127.60, 126.93, 126.87, 126.65, 126.29, 125.62, 125.38, 125.32, 123.54, 115.34. ELEM. ANAL. Calcd. for $C_{48}H_{33}Br_2N$: C, 73.55; H, 4.22; N, 1.76. Found: C, 73.36; H, 4.19; N, 1.69.

Synthesis of the polymer

Synthesis of poly(9,9-dioctyl)-2,7-fluorene-co -N-4-(2,3,4,5-tetraphenyl)diphenyl-4,4′-diphenylamine (PFT-TPP)

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.321 g, 0.5 mmol), *N*,*N*-bis(4-bromophenyl)-4′-[(2,3,4,5-tetraphenyl)phenyl]phenylamine (**5**) (0.392 g, 0.5 mmol), palladium acetate ($Pd(OAc)_2$) (3 mg) and tris(cyclohexyl)phosphine (6 mg) were dissolved in 8 mL of degassed toluene. Then the Et_4NOH aqueous solution (20%, 2 mL) was added via syringe. The reaction mixture was bubbled with N_2 for 30 min and stirred at refluxing for 3 days under nitrogen. This mixture was cooled down to room temperature and poured into 200 mL of methanol. The resulted precipitate was recovered by filtration and purified by silica column chromatography with toluene as eluent to remove small molecules complex and catalyst residue. The final product was obtained as pale-yellow fibrous solid after vacuum dried at 50 °C overnight (0.43 g, 92%). FT-IR (KBr, cm^{-1}): 3055, 3027, 2924, 2582, 1599, 1510, 1463, 1318, 1287, 1183, 815, 762, 699, 549. ^{1}H NMR (400 MHz, $CDCl_3$). δ (ppm) 7.76–7.74 (d, 2H), 7.63 (s, 1H) 7.59–7.55 (m, 6H), 7.21–7.16 (m, 8H), 7.08–6.80 (m, 22H), 2.17–2.03 (m, 4H, fluorene –CH_2–), 1.54–0.88 (m, 30H, alkyl H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.42, 146.72, 145.90, 141.79, 141.74, 140.67, 140.48, 140.37, 140.17, 140.03, 139.81, 139.37, 139.17, 137.29, 135.90, 131.68, 131.59, 131.52, 131.10, 130.92, 130.01, 127.81, 127.62, 126.95, 126.67, 126.29, 125.65, 125.37, 124.54, 124.31, 123.35, 120.95, 119.94, 55.26, 40.54, 31.80, 30.08, 29.24, 29.14, 23.86, 22.63, 17.97, 14.15. ELEM. ANAL. Calcd. for $C_{77}H_{73}N$: C, 91.30; H, 7.21; N, 1.38. Found: C, 90.56; H, 7.09; N, 1.25.

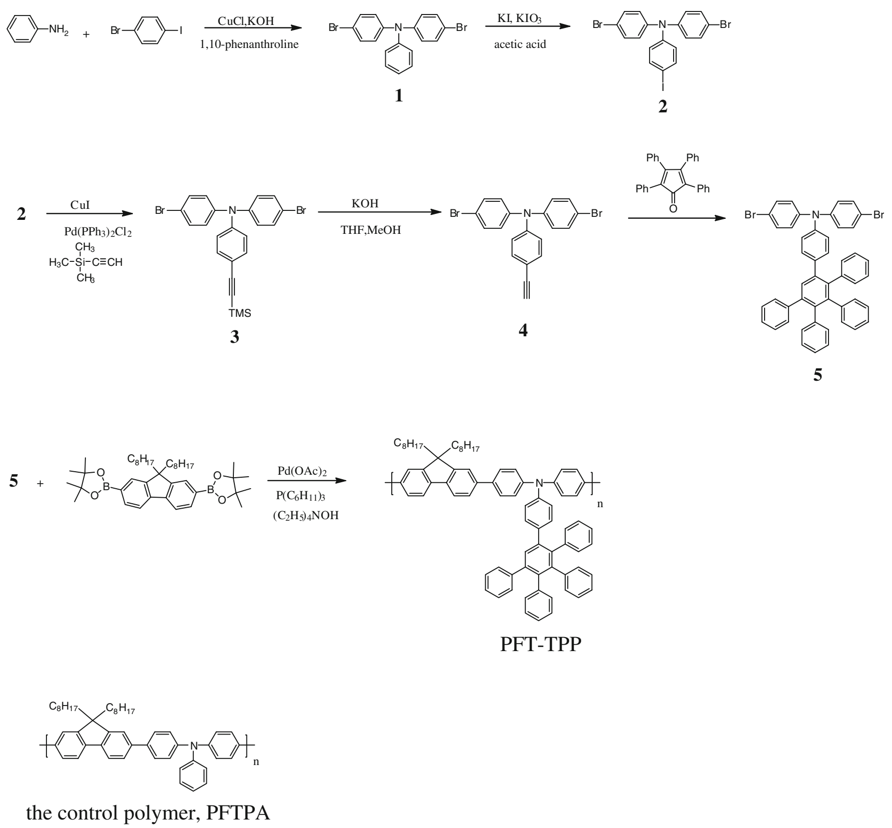
Results and discussion

Synthesis and characterization

The synthetic procedure used to prepare the intermediates and the polymer PFT-TPP is outlined in Scheme 1. A type of modified Ullmann reaction [31], with the catalyst system of phenanthroline, CuCl, and KOH, was utilized to synthesize the intermediate *N*,*N*-bis(4-bromophenyl)aniline (**1**). Preparation of compound **1** has been achieved previously by the direct bromination of triphenylamine [10, 32]. However, in these previous studies, the purification process was complicated by difficulty in the extraction of the desired di-brominated product from the crude products (also containing mono-, and tri-brominated triphenylamines). The Ullmann reaction used in our experiment is based on the much higher reactivity of an iodo-site as compared to that of a bromo-site, which results in the coupling reaction happening exclusively at the iodo-substituted position. The absence of extraneous mono- and tri-brominated byproducts made purification much simpler. Using potassium iodide–potassium iodate in acetic acid [33], the *N*,*N*-bis(4-bromophenyl)aniline (**1**) was successfully iodinated at the remaining *para*-position on the triphenylamine group. Palladium-catalyzed Sonogashira coupling reaction [34] was then employed to introduce an ethynyl group to the iodo-position in *N*,*N*-bis(4-bromophenyl)-4′-iodophenylamine (**2**) to produce *N*,*N*-bis(4-bromophenyl)-4′-(trimethylsilylethynyl)phenylamine (**3**). At room temperature, the coupling reaction happened preferentially at the iodo-position over the bromo-position, due to the much higher reactivity of the former in the Sonogashira reaction. The next product, *N*,*N*-bis(4-bromophenyl)-4′-(ethynyl)phenylamine (**4**), was obtained by the desilylation [25] of compound **3** using KOH as a base in a THF/methanol medium. The Diels–Alder reaction [25] of compound **4** with tetraphenylcyclopentadienone in refluxing *o*-xylene successfully generated the target product, *N*,*N*-bis(4-bromophenyl)-4′-[(2,3,4,5-tetraphenyl)phenyl]phenylamine (**5**) in very high yield.

The copolymer, poly(9,9-dioctyl)-2,7-fluorene-*co*-*N*-4-(2,3,4,5-tetraphenyl)-diphenyl-4,4′-diphenylamine (PFT-TPP), and the control polymer, poly(9,9-dioctylfluorene-*co*-4,4′-triphenylamine) (PFTPA), were synthesized by a palladium-catalyzed Suzuki coupling reaction [35]. Both polymers are readily soluble in common organic solvents, such as chloroform, toluene, chlorobenzene, and tetrahydrofuran (THF). The number-average molecular weights (M_n) of these two polymers, as determined by GPC against polystyrene standards, were 12,000 for PFT-TPP and 9,000 for PFTPA, with the polydispersity indices of 2.0 and 2.1, respectively. The chemical structures of all intermediates and polymers were verified by NMR, FT-IR, and elemental analyses.

Figure 1 shows the ^{1}H NMR (Fig. 1a) and ^{13}C NMR (Fig. 1b) spectra of PFT-TPP. As indicated in Fig. 1a, a signal with a unique single splitting profile, which can be assigned to the remaining proton located at the tetraphenyl-substituted phenyl group (labeled “h” in Fig. 1a) in the pendant of PFT-TPP, appears at δ 7.63 ppm. The signal at δ 7.76–7.74 ppm corresponds to the protons in the fluorene moiety (labeled “c” in Fig. 1a). The other aromatic and the aliphatic protons are also well-resolved and fairly well assignable. The chemical structure of



Scheme 1 Synthetic route of the polymer PFT-TPP

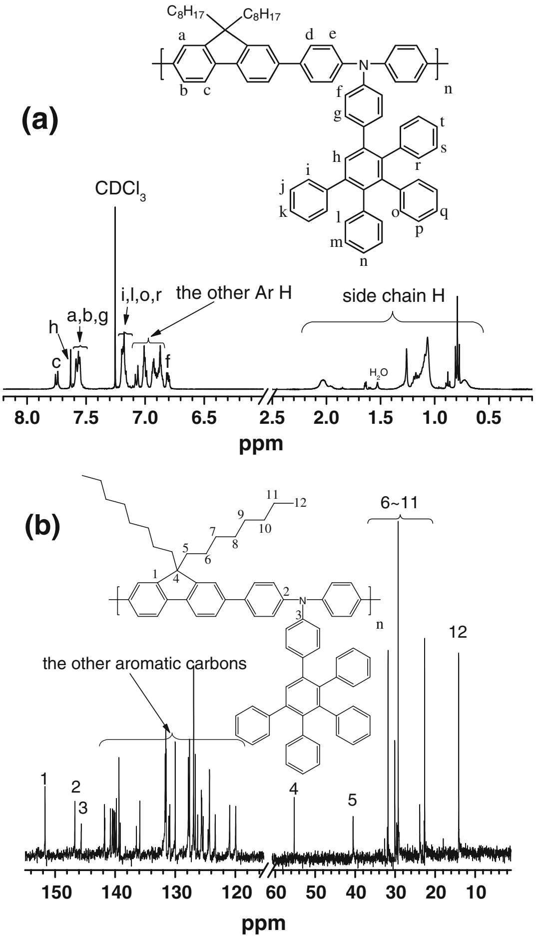
PFT-TPP can also be assessed by its ^{13}C NMR spectrum. As seen in Fig. 1b, the signals at δ 151.42, 146.72, and 145.90 ppm correspond to the carbons located in the fluorene (labeled “1” in Fig. 1b) and the triphenylamine (labeled “2” and “3” in Fig. 1b) segments, respectively. The resonances of the side chain carbons in the high field region are also in good agreement with the chemical structure.

The thermal properties of PFT-TPP were evaluated by the thermogravimetric analysis (TGA) (at a temperature range of 25–800 °C in air). TGA revealed an onset decomposition temperature of ca. 420 °C, suggesting that the PFT-TPP polymer possesses very good thermal stability—certainly sufficient to meet the requirements for application in OLEDs.

Optical properties of PFT-TPP

The optical properties of PFT-TPP were measured both in solution and in solid state. Figure 2 shows the UV–vis spectra of PFT-TPP in THF solution (Fig. 2a) and as a solid film (Fig. 2b). The corresponding UV–vis spectra of PFTPA are also

Fig. 1 ^{1}H NMR (**a**) and ^{13}C NMR (**b**) spectra of PFT-TPP



depicted for comparison. The concentration of the solutions was controlled at about 1×10^{-5} M, based on the polymer repeat unit. Transparent and uniform films of PFT-TPP and PFTPA were prepared on glass substrates by spin-casting from their chloroform solutions at room temperature. As shown in Fig. 2a, despite the slightly red-shifted absorption profile of PFT-TPP when compared to that of PFTPA, the absorption maxima of both polymers appeared at 382 nm. The maximum absorption of the PFT-TPP and PFTPA films was slightly blue-shifted (ca. 4 nm) relative to that of their corresponding THF solutions, and both polymers showed absorption peaks at 378 nm (Fig. 2b). The absorption of the PFT-TPP and PFTPA films starting at 428 and 427 nm, respectively, corresponded to optical bandgaps of ca. 2.90 eV for both polymers.

The PL spectra of the two polymers in THF ($\sim 1 \times 10^{-5}$ M) (Fig. 3a) and in solid state (Fig. 3b) are illustrated in Fig. 3. At an excitation of 380 nm, the solutions of PFT-TPP and PFTPA emitted blue light, with the maximum emission

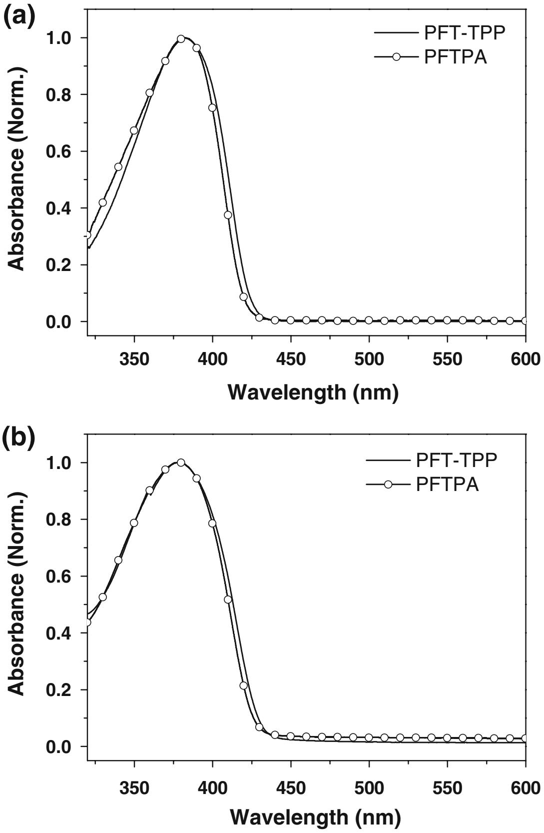


Fig. 2 UV–vis absorption spectra of PFT-TPP and PFTPA in THF (a) and in films (b)

appearing at 447 and 441 nm, respectively. The PL emission of PFT-TPP and PFTPA films peaked at 444 and 440 nm, accompanied by the appearance of shoulder emissions at 455 and 452 nm, respectively. As indicated in Figs. 2 and 3, no significant influence was seen on the electronic conjugation of PFT-TPP by the introduction of the bulky (2,3,4,5-tetraphenyl)phenyl pendant. The absorption and the emission maxima of the films of both polymers were slightly blue-shifted compared to their corresponding solutions, suggesting a weak aggregation effect in their solid states. The absolute PL quantum efficiencies of the films of PFT-TPP and PFT-TPA were 5.0 and 3.2%, respectively.

Although the relatively low quantum efficiency of PFT-TPP would make it unfavorable for its application as an emitter in a PLED, further improvement might be realized by tuning the composition ratio of the pendant-containing triphenylamine moieties in the polyfluorene backbones. According to a previous report, for polymers with the same building blocks, the alternating connection used here may not necessarily be optimal—superior properties might be achieved by modification of the composition of the co-monomers [36]. The synthesis results and the optical and thermal properties of PFT-TPP and PFTPA are summarized in Table 1.

Fig. 3 PL spectra of PFT-TPP and PFTPA in THF (**a**) and in films (**b**)

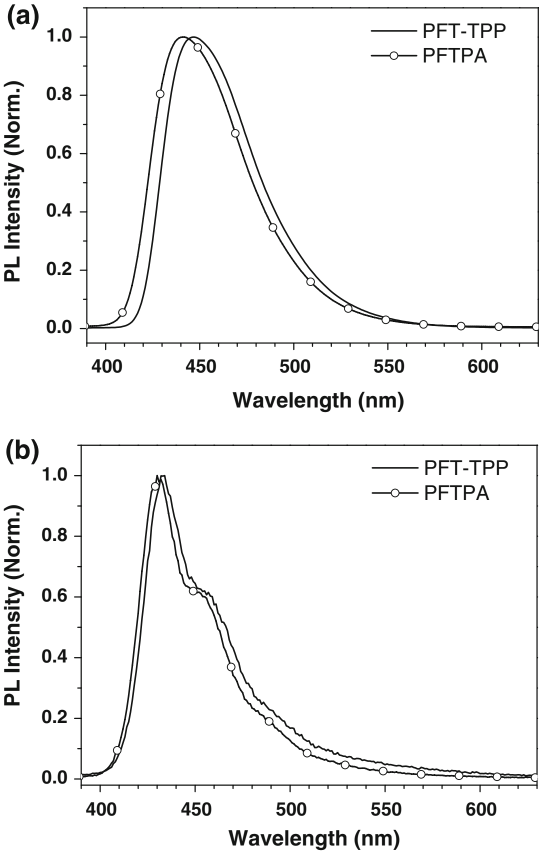


Table 1 Synthesis results, optical data and thermal properties of PFT-TPP and PFTPA

Polymer	M_n^a	M_w/M_n	T_d (°C)^b	λ_{max} (nm; UV–vis)		λ_{EM}^c (nm; FL)		Φ_f^d
				In THF	In film	In THF	In film	
PFT-TPP	12,000	2.0	423	382	378	447	444	5.0
PFTPA	9,000	2.1	430	382	378	441	440	3.2

[a] Determined by GPC (with polystyrene standards)

[b] The decomposition onset temperature obtained by TGA

[c] Position of the emission peak from PL data

[d] Absolute quantum yield of the polymer films, measured by using a calibrated integrating sphere at an exciting wavelength of 325 nm

Electrochemical property

The electrochemical behaviors of PFT-TPP and PFTPA were investigated by cyclic voltammetry (CV), and the corresponding CV curves are depicted in Fig. 4. The oxidation and deoxidation processes were readily detected, whereas the

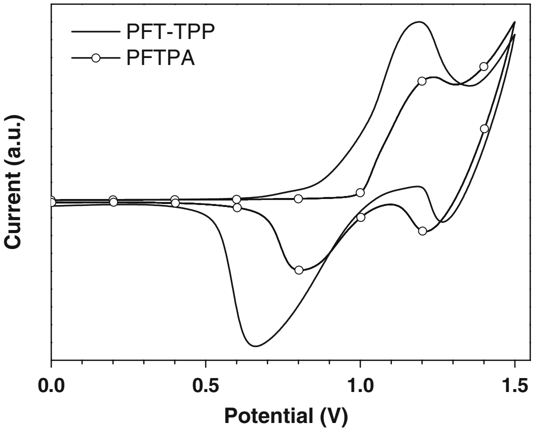


Fig. 4 Cyclic voltammograms of polymer films coated on platinum electrodes in 0.1 mol L^{-1} Bu_4NPF_6, CH_3CN solution

Table 2 Electrochemical properties of PFT-TPP and PFTPA in solid films

Polymers	Optical band gap[a] (eV)	E_{ox} (V)	E_{HOMO} (eV)	E^{b}_{LUMO} (eV)
PFT-TPP	2.90	0.90	−5.30	−2.40
PFTPA	2.90	0.96	−5.36	−2.46

[a] Estimated from the onset wavelength of optical absorption in the solid state film

[b] Calculated from the HOMO level and optical band gap

corresponding reduction processes were not observed, even after several trials. As seen in Fig. 4, the CV behaviors of PFT-TPP and PFTPA showed a strong resemblance to each other. The oxidative processes of PFT-TPP and PFTPA started at 0.90 and 0.96 V, respectively, which corresponds to the p-doping process of the triphenylamine segment in the polymer backbones. The p-doping processes of both polymers were almost completely reversible, suggesting that they possess excellent electrochemical stability.

The energy levels of the highest occupied molecular orbital (HOMO) of PFT-TPP and PFTPA can be estimated from the corresponding onsets of their oxidation waves. These were calculated according to an empirical formula, $E_{HOMO} = -e(E_{ox} + 4.4)$ (eV) [37], to be −5.30 and −5.36 eV, respectively. The levels of the lowest unoccupied molecular orbital (LUMO) can be estimated by subtracting their optical bandgaps from the corresponding HOMO energies. These were calculated to be −2.40 and −2.46 eV for PFT-TPP and PFTPA, respectively. The electrochemical properties of the two polymers as solid films are summarized in Table 2.

Conclusions

We have synthesized a type of conjugated polymer based on alternating units of fluorene and a bulky pendant-bearing triphenylamine, PFT-TPP, coupled through

Suzuki reaction. This copolymer exhibited high solubility in common organic solvents, good processability, and high thermal stability. The UV–vis absorption, emission, and the electrochemical properties of PFT-TPP were characterized. The introduction of the (2,3,4,5-tetraphenyl)phenyl pendant to the polymer backbone of PFT-TPP had no appreciable influence on the optical or electrochemical properties, as determined by comparison with a control polymer, PFTPA. The PFT-TPP polymer shows good potential as a blue-emitting and hole-transporting material for use in OLED applications.

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