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Synthesis and optoelectronic properties of thermally cross-linkable hole-transporting poly(fluorene-*co*-triphenylamine)

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ABSTRACT

This paper describes the synthesis of a new thermally cross-linkable hole-transporting poly(fluorene-*co*-triphenylamine) (**PFTV**) by Suzuki coupling reaction and its application in polymer light-emitting diodes (PLEDs). The characteristics of **PFTV** were analyzed by ¹H NMR, differential scanning calorimetry, optical spectroscopy, cyclic voltammetry, and atomic force microscopy. Its HOMO level lies between those of PEDOT:PSS and poly(9,9-dioctylfluorene), forming a stepwise energy ladder to facilitate hole-injection. Multilayer device with thermally cross-linked **PFTV** as hole-transporting layer (ITO/PEDOT:PSS/HTL/**PFO**/LiF/Ca/Al) was readily fabricated by successive spin-coating processes, its maximum luminance efficiency (2.27 cd/A) was significantly higher than that without **PFTV** layer (0.50 cd/A). In addition, the **PFTV** was successfully applied as host for red-emitting Ir(piq)₂acac to obtain a device with moderate performance (5300 cd/m² and 2.64 cd/A). The **PFTV** is a promising hole-transporting material for the fabrication of multilayer PLEDs by wet processes as well as a potential host for phosphorescent PLEDs.

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1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted much attention, since the first discovery of electroluminescene of poly (p-phenylenevinylene) (PPV) in 1990, due to their potential applications in large area flat panel displays and solid-state lighting [1-5]. Organic materials in PLEDs have some advantages such as potentially low cost, facile processing by spin-coating and ink-jet printing methods. A lot of conjugated polymers have been extensively investigated, such as poly(p-phenylenevinylene) (PPV) [1], polyfluorene (PF) [6] and their derivatives. PF and its derivatives are promising blue-light-emitting materials widely used in PLEDs because of its excellent thermal and chemical stability and high photoluminescence (PL) quantum yield [7–9]. However, the lower highest occupied molecular orbital (HOMO) level of PF ($E_{HOMO} = -5.8 \text{ eV}$) creates a high hole-injection barrier, which lead to imbalance in charges injection [10,11]. This characteristic ultimately results in low efficiency obtainable for its polymeric light-emitting diodes.

To solve this problem, in general two strategies have been adopted, one is through appropriate design of chemical structure and the other is via adequate modification of device structure. For the first strategy, the incorporation of hole-transporting moieties on a main or side chain, such as carbazole or triphenylamine, is usually adopted to improve hole-injection from anode [12–18]. For the second strategy, multilayer devices are required and fabricated by adding an extra hole-transporting layer (HTL) to reduce the hole-injection barrier from anode [19–24]. Several polymers have been reported as suitable materials for HTL between poly(styrenesulphonate):poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) and emitting layer (EML), such as poly(*N*-vinylcarbazole) (PVK) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl))diphenylamine)] (TFB) [23-26]. The hole-transporting layer (HTL) effectively improves the device efficiency of multilayer PLEDs. However, for multilayer polymer devices the HTL layer may be dissolved or destroyed by the solution of emitting layer during subsequent spin-coating. Therefore, the homogeneity and actual thickness of the HTL cannot be controlled at will. This will lead to poor reproducibility in the fabrication of multilayer devices by solution processes. Accordingly, solvent resistance of the HTL layer should be high enough to prevent the dissolution during subsequent coating. An effective way to increase the solvent resistance of a polymer is forming as a three dimensional network structure, which can be attained by thermal or photo-initiated cross-linking reaction [27-36]. Moreover, the solvent resistance increases with the increase of cross-linking density. Therefore, the HTL applicable in multilayer PLEDs fabricated by solution-processes should possess not only a proper energy level lying between anode and emitting layer to facilitate hole-injection but also high solvent resistance to avoid being dissolved during subsequent spincoating of the emitting layer.





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In the present study we synthesized a new thermally crosspoly(fluorene-co-triphenylamine) linkable hole-transporting (PFTV) by Suzuki coupling reaction, incorporated with pendent styryl groups which is thermally reactive. The PFTV is composed of hole-transporting triphenylamine groups and fluorenes substituted with nonsymmetric and bulky aromatic groups at C-9 position. This molecular design is expected to enhance thermal and chemically stability, good film-forming properties and device efficiency. Moreover, fabricating multilayer PLEDs with PFTV as hole-transporting layer will be highly reproducible due to its thermally crosslinking ability. The multilayer device with cross-linked PFTV as HTL shows significantly enhanced emission efficiency than those with uncross-linked PFTV as HTL or without the PFTV layer. Furthermore, the **PFTV** was effectively applied as host for red-emitting Ir (pig)₂acac, indicating that it acts both as hole-transporting and host materials in PLEDs. These results demonstrate that the new **PFTV** is a promising hole-transporting and host material for optoelectronic devices.

2. Materials and methods

2.1. Materials and characterization

Tri(4-bromophenyl)amine (2) [37] and 4-(3-methylpropyl)-N,Nbis(4-bromophenyl)aniline (5) [38,39] were synthesized according to the procedures reported previously. 9,9-diarylfluorene-2,7diboronic acid bispinacol ester (4) and poly(9,9-dioctylfluorene) (PFO) were prepared according to our previously reported procedures [40]. All reagents and solvents were purchased from Acros. TCI, Aldrich, Lancaster Chemicals Co. and used without further purification. All the solvents such THF and acetonitrile were dried with appropriate drying agents (Na or CaCl₂), then distilled under reduced pressure and stored over 4 Å molecular sieves before use. The polymerization catalyst was tetrakis(triphenylphosphine) palladium [Pd(PPh₃)₄] procured from Strem. Newly synthesized compounds were identified by ¹H NMR, ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis (EA). ¹H NMR and ¹³C NMR spectra were recorded with Bruker AVANCE-400 and 500 NMR spectrometers respectively, and the chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. Mass and elemental analysis were carried out on a JEOL JMS-700 spectrometer and Heraus CHN-Rapid elemental analyzer, respectively. The FT-IR spectra were measured as KBr disk using a Fourier transform infrared spectrometer, model 7850 from Jasco. Molecular weight and molecular weight distribution of the polymer were determined by a gel permeation chromatograph (GPC) using THF as an eluent at a flow rate of 1 mL/min at 40 °C. Monodisperse polystyrene standards were used for molecular weight calibration. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 20 °C/min, using a PerkinElmer TGA-7 thermal analyzer. Thermal curing behaviors and thermal transitional properties of the polymer were investigated using a differential scanning calorimeter (DSC), Mettler DSC 1, at a heating rate of 10 °C/min. Absorption spectra and photoluminescence (PL) spectra were measured with a Jasco V-550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammograms were recorded using a voltammetric analyzer (model CV-50W from Bioanalytical Systems, Inc.) under nitrogen atmosphere. The measuring cell was consisted of a polymer-coated ITO glass as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M (n-Bu)₄NClO₄ as electrolyte. The energy levels were calculated using ferrocene (FOC) as standard (-4.8 eV with respect to vacuum level which is defined as zero) [41,42]. An atomic force microscope (AFM), equipped with a Veeco/ Digital Instrument Scanning Probe Microscope (tapping mode) and a Nanoscope IIIa controller, was used to examine surface morphology and to estimate thickness and root-mean-square (rms) roughness of deposited films. The film thickness of hole-transporting and emitting layers was measured by surface profiler, α -step 500.

2.2. Synthesis of monomer (3) and copolymer (PFTV)

2.2.1. Synthesis of N,N-bis(4-bromophenyl)-p-(4-vinylphenyl) aniline (**3**)

Tri(4-bromophenyl)amine (2, 4.82 g, 10 mmol), p-vinylphenylboronic acid (1.15 g, 5 mmol) and (PPh₃)₄Pd(0) (0.144 g, 0.13 mmol) were dissolved in a mixture consisting of tetrahydrofuran (THF: 20 mL), aqueous solution of 2 M K₃PO₄ (11 mL). The mixture was first purged with Argon and stirred at 100 °C for 48 h under vigorous stirring. It was poured into water (50 mL) and extracted twice with dichloromethane (250 mL). The combined organic extracts were dried (MgSO₄) and concentrated by rotary evaporation. Further purification by column chromatography on silica gel (ethyl acetate/n-hexane) afforded product 3 as white solids (yield: 65%, melting point: 160-161 °C). FT-IR (KBr pellet, cm⁻¹): *v* 719, 815, 898, 1068, 1286, 1317, 1484, 1521, 1579, 1602, 1621, 3033, 3054, 3081. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.54–7.45 (m, 6H, Ar-H), 7.37–7.35 (d, 4H, Ar-H, J = 8 Hz), 7.11–7.09 (d, 2H, Ar-H, J = 8 Hz), 6.99–6.97 (d, 4H, Ar-H, J = 8 Hz), 6.78–6.71 (dd, 1H, $= CH^{-1}$, $J_1 = 16$ Hz, $J_2 = 16$ Hz), 5.80-5.76 (d, 1H, $= CH_2$, J = 16 Hz), 5.30–5.26 (d, 1H, = CH₂, J = 16 Hz). ¹³C NMR (500 MHz, CDCl₃, ppm): δ 146.38, 146.24, 139.68, 136.45, 136.39, 135.82, 132.43, 127.88, 126.74, 126.69, 126.02, 125.63, 124.45, 115.74, 113.8. ELEM A_{NAL} Calcd. for C₂₆H₁₉Br₂N (%): C, 61.81; H, 3.79; N, 2.77. Found: C, 61.70; H, 3.85; N, 2.71. EI-MS (*m*/*z*): calcd: 504.99; found: 505.00.

2.2.2. Synthesis of poly(fluorene-co-triphenylamine) (**PFTV**)

The synthesis of poly(9,9-dioctylfluorene) (PFO) and copolymer PFTV was carried out using a palladium-catalyzed Suzuki coupling reaction. For instance, purified N,N-bis(4-bromophenyl)p-(4-vinylphenyl)aniline (3: 0.304 g, 0.6 mmol), 9,9-diarylfluorene-2,7-diboronic acid bispinacol ester (4: 3.843 g, 5 mmol), 4-(3-methylpropyl)-*N*,*N*-bis(4-bromophenyl)aniline (5: 2.02 g, 4.4 mmol) and (PPh₃)₄Pd(0) (0.104 g, 0.09 mmol) were dissolved in a mixture consisting of THF (30 mL) and aqueous solution of 2 M K₃PO₄ (16 mL). The mixture was first purged with Argon and then stirred at 100 °C for 72 h under vigorous stirring. Finally, monomer 4 and 1-bromo-4-tert-butylbenzene were added to the mixture to end-cap the polymer chain. The mixture was poured into a large amount of methanol; the appeared solid was collected by filtration and washed successively with methanol, 2-propanol and hexane, followed by Soxhlet extraction with acetone to remove trace oligomers. The residual palladium catalyst was removed by stirring together with a silica gel (Silicycle, Si-Thiol) in toluene. Then the solution was further extracted with de-ionized water three times to reduce the concentration of metal ions. It was then poured into a large amount of methanol to afford lightyellow fiber of PFTV (yield: 75%). The PFTV was soluble in conventional organic solvents such as toluene, xylene, THF and chloroform. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.78–7.76 (d, Ar-H, J = 8 Hz), 7.58–7.56 (d, Ar-H, J = 8 Hz), 7.49–7.44 (m, Ar-H), 7.26-7.04 (m, Ar-H), 6.94-6.87 (m, Ar-H), 6.64-6.62 (m,=CH-), 5.80–5.76 (d,=CH₂, J = 16 Hz), 5.27–5.24 (m,=CH₂, J = 12 Hz), 3.94-3.91 (t, $-OCH_2-$, J = 12 Hz), 2.58-2.56 (m, 1H, -CH-), 2.20(s, 3H, -CH₃), 2.10 (s, 3H, -CH₃), 1.80-0.83 (m, -CH₂- and -CH₃). ¹³C NMR (500 MHz, CDCl₃, TMS, 25 °C): δ 155.86, 152.83, 147.04, 142.79, 139.60, 138.83, 136.63, 134.63, 134.42, 132.36, 131.31,

130.58, 127.47, 126.62, 126.25, 125.93, 125.08, 124.20, 120.34, 110.32, 66.17, 65.28, 40.98, 39.19, 37.26, 36.32, 31.34, 29.91, 27.93, 24.65, 22.67, 22.58, 21.81, 21.24, 19.73, 16.58, 12.27. ELEM. ANAL. Calcd. for **PFTV** (%): C, 88.43; H, 7.67; N, 1.71. Found (%): C, 87.64; H, 7.71; N, 1.28.

2.3. Fabrication and characterization of light-emitting devices

Multilaver light-emitting diodes [ITO/PEDOT:PSS/HTL/PFO/LiF/ Ca/Al] or phosphorescent light-emitting diodes [ITO/PEDOT:PSS/ PFTV:Ir(piq)₂acac/Ca/Al] were fabricated to investigate their optoelectronic characteristics. The ITO-coated glass substrate was washed successively in ultrasonic baths of neutraler reiniger/deionized water (1:3 v/v) mixture, de-ionized water, acetone and 2-propanol, followed with treatment in a UV–Ozone chamber. A thick PEDOT:PSS laver was spin-coated on top of the freshly cleaned ITO glass and annealed at 150 °C for 15 min in a dust-free atmosphere. The PFTV solutions were filtered through a syringe filter $(0.2 \,\mu\text{m})$ before the spin-coating. The hole-transporting layer (HTL) was formed by spin-coating a solution of **PFTV** in toluene (10 mg/mL, 2000 rpm) on top of the PEDOT:PSS layer and thermally treated at 230 °C for 30 min under nitrogen atmosphere. Then the emitting layer (EML) was spin-coated onto the HTL. The actual thickness of HTL and EML is 40 and 70 nm, respective. Finally, a thick layer of cathode was deposited by successive thermal evaporation of LiF (1 nm), Ca (50 nm) and Al (100 nm) under 110⁻⁶ Torr. The luminance versus bias, current density versus bias, and emission spectra of the PLEDs were recorded using a combination of Keithley power source (model 2400) and Ocean Optics usb2000 fluorescence spectrophotometer. The fabrication of the devices was done in ambient conditions, with the following performance tests conducted in a glove-box filled with nitrogen.

3. Results and discussion

3.1. Synthesis and characterization

The hole-transporting poly(fluorene-co-triphenylamine)(**PFTV**) was synthesized by the palladium-catalyzed Suzuki coupling of 9,9diarylfluorene-2,7-diboronic acid bispinacol ester (4) and dibromotriphenylamine derivatives (3, 5) as shown in Scheme 1. The emitting poly(9,9-dioctylfluorene) (PFO) was also synthesized by the Suzuki coupling reaction. Tri(4-bromophenyl)amine (2) and 4-(3-methylpropyl)-*N*.*N*-bis(4-bromophenyl)aniline (5) were synthesized according to the procedures reported previously [37–39]. 9.9-diarylfluorene-2.7-diboronic acid bispinacol ester (4) and poly (9,9-dioctylfluorene) (PFO) were prepared according to our previously reported procedures [40]. Monomer 3 was synthesized by the Suzuki coupling of *p*-vinylphenylboronic acid with stoichiometric amount of tri(4-bromophenyl)amine (2), which was obtained by complete bromination of triphenylamine with N-bromosuccinimide (NBS). Chemical structure of monomer 3 was satisfactorily confirmed by ¹H NMR, ¹³C NMR spectra, elemental analysis, and mass spectrometry. ¹H NMR spectrum of **3** verifies the characteristic chemical shifts at 6.78-6.71 ppm and 5.26-5.80 ppm assigned to protons of the vinyl substituents ($=CH_2$ and $=CH_-$). The structure of **PFTV** was satisfactorily characterized by its ¹H NMR, ¹³C NMR spectra (Fig. S1 in Supporting Information) and elemental analysis. The actual composition of pendent styryl group is ca. 5 mol%, as estimated from the areas of the peaks at 5.24–5.80 ppm



Scheme 1. Synthesis of monomer 3 and copolymer PFTV, and chemical structure of poly(9,9-dioctylfluorene (PFO).

 Table 1

 Thermal and electrochemical properties of PFTV and PFO.

	$T_g \ (^\circ C)^a$	$T_d (^{\circ}C)^b$	E_{ox} vs. FOC (V) ^c	$E_{HOMO} (eV)^d$	E _{LUMO} (eV) ^e	$E_g^{opt} (eV)^f$
PFTV	225	419	0.47	-5.27	-2.41	2.86
PFO	68	432	0.90	-5.70	-2.77	2.93

 $^{\rm a}$ Determined by differential scanning calorimetry (DSC) at a heating rate of 10 $^\circ C/min.$

 $^{\rm b}$ The temperature at 5 wt% loss in nitrogen atmosphere, measured by TGA. $^{\rm c}$ $E_{FOC}=0.47$ V vs. Ag/AgCl.

 $^{d}E_{HOMO} = -(E_{ox, FOC} + 4.8) \text{ eV}.$

 $E_{\text{HOMO}} = -(E_{\text{OX}, \text{FOC}} + E_{\text{HOMO}})$

^f Band gaps obtained from onset absorption (λ_{onset}): E_g = 1240/ λ_{onset} .

 $(=C\underline{H}_2)$ and 3.91 ppm $(-OC\underline{H}_2-)$. The characteristic chemical shifts at 5.24–5.80 ppm confirm the existence of pendent styryl groups, from which thermally cross-linkable character can be expected. The **PFTV** and **PFO** are soluble in common organic solvents such as toluene, THF, and chloroform. The weight-average molecular weight (M_w) of **PFTV** and **PFO** was 6.9×10^4 and 14.4×10^4 , respectively, with the polydispersity indexes (PDIs) being 1.8, as determined by gel permeation chromatography using monodisperse polystyrenes as calibration standards.

3.2. Thermal cross-linking properties and surface morphology of **PFTV**

Since the copolyfluorene (PFTV) contains reactive pendent styryl groups which will give rise to networks structure (cross-linking) under proper thermal treatment. Thermal cross-linking and thermal stability characteristics of **PFTV** were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The thermal decomposition temperature (T_d. 5% weight loss) of PFTV is 419 °C under nitrogen atmosphere, indicating that the PFTV is highly thermal stable (Table 1). As shown in Fig. 1 (inset), during the first DSC heating scan of monomer 3 a clear-cut melting point at about 161 °C is observed, followed closely by an exothermic peak around 163 °C. The exothermic peak is attributed to the reaction of styryl groups which is induced by the melt of **3**. Thermal cross-linking conditions of **PFTV** were first determined by a similar DSC heating scan to 300 °C (Fig. 1). During the first heating scan, PFTV showed broad an exothermic peak around 230 °C, in which the exotherm starts at about 210 °C. This exothermic peak (230 °C) of **PFTV** is much higher than that of monomer **3** (163 $^{\circ}$ C), which is ascribed to high



Fig. 1. DSC traces of **PFTV** at a heating rate of 10 °C/min. The first scan was used to observe the reaction heat of styryl groups. The inset shows the DSC trace of monomer **3** at a heating rate of 10 °C/min.



Fig. 2. Absorption spectra of pristine and cross-linked **PFTV** films: (-) before and (---) after spin-coated with pure toluene. The cross-linking was conducted at 230 °C or 240 °C for 30 min under nitrogen atmosphere. The inset in (b) shows the absorption spectra of **PFTV** film containing 1 wt% of dicumyl peroxide (DCP).

glass transition temperature of **PFTV** comprising rigid aromatic main chain structure and bulky aromatic substituents at the C-9 position. The exothermic heat (35.25 J/g) is attributable to the thermal crosslinking reaction of the pendent styryl groups. No obvious exotherm is observed in the second heating scan, indicating the cross-linking has been completed during the first scan. Furthermore, the glass transition temperature (T_g) of the cured **PFTV** is about 225 °C with no detectable crystallization and melting transitions, suggesting that it is basically an amorphous material. The high T_g is a highly desirable property for polymers used in PLEDs, since it prevents the detrimental crystallization process during device operation or thermal annealing which deteriorates long-term morphological stability.

Solvent resistance of the cured **PFTV** film was investigated by the absorption variations (300–700 nm) before and after washing

with a good solvent (toluene). As shown in Fig. 2, the absorption spectrum of the pristine **PFTV** film disappears almost completely after rinsing with toluene, meaning that the **PFTV** film is dissolved out during spin-coating process. However, the solvent resistance of **PFTV** was enhanced by the thermal curing processes. For instance, the remaining absorption intensity of the thermally cross-linked **PFTV** film (at 230 °C for 30 min) was about 27% after rinsing with toluene. Moreover, its solvent resistance is further promoted when cured at higher temperature (240 °C for 30 min), i.e., more than 48% of absorption intensity was remained after rinsing with toluene. In addition, the degree of cross-linking could be increased by adding dicumyl peroxide (DCP) as cross-linking agents. The remaining absorption intensity of thermally cross-linked PFTV film, added with DCP (1 wt%) and cured at 230 °C for 30 min, was about 37% after rinsing with toluene. These results indicate that both higher curing temperature and cross-linking agent are effective in increasing cross-linking density, which can be evidenced by elevated glass transition temperatures [32]. Therefore, the solutionprocessable and thermally cross-linkable characteristics of PFTV are useful to fabricate multilayer PLEDs by spin-coating processes.

To achieve high performance in multilayer PLEDs, it is imperative to obtain highly homogeneous film for each layer. Homogeneous film is a prerequisite to obtain PLEDs with high device performance and long lifetime. The morphology of PFTV spincoated onto ITO substrate, before and after thermal curing, was investigated using an atomic force microscope (AFM). As shown in Fig. 3. the **PFTV** film exhibits a uniform surface morphology with no observable pinhole or aggregate after thermal cross-linking at 230 °C for 30 min. Moreover, the average root-mean-square (rms) roughness of the cross-linked PFTV film surface is 0.85 nm (0.88 nm, 0.82 nm, 0.85 nm), which is slightly lower than 0.94 nm of pristine film (0.92 nm, 0.99 nm, 0.90 nm). According, the thermal treatment not only promotes solvent resistance but also smoothes out the film surface of PFTV. Most of the reported thermally curable HTLs are low molecular weight compounds [28,31–33], although polymers with trifluorovinyl ether pendent groups were also investigated [29,33]. The film-forming property and thermal stability of low molecular weight HTLs are usually inferior to polymeric counterparts. Moreover, thermal cross-linking of the polymers containing trifluorovinyl ether pendent groups required both high temperatures (>225 °C) and long times (1–2 h). Therefore, the thermally cross-linkable PFTV should be a potential candidate for hole-transporting materials from the viewpoint of thermal property and processing feasibility.



Fig. 4. The energy level diagrams of PFTV, PFO, PEDOT:PSS and Calcium electrode.

3.3. Electrochemical properties

Cyclic voltammetry (CV) is a commonly used technique to investigate electrochemical properties of conjugated polymers [43,44]. An ITO glass coated with PFTV was used as the working electrode, supporting in anhydrous acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate $[(n-Bu)_4NClO_4]$, to measure its CV. The highest occupied molecular orbital (HOMO) which corresponds to ionization potential (IP) can be estimated from the onset oxidation potential (Eox) revealed in CV by the equation $E_{HOMO} = -(E_{ox} + 4.8)$ eV. The lowest unoccupied molecular orbital (LUMO) level is calculated by $E_{LUMO} = -e(E_{HOMO} + E_{g}^{opt})$, where the optical band gap (E_g^{opt}) is estimated from onset absorption. The HOMO and LUMO levels of PFTV are estimated to be -5.27 eV and -2.41 eV, respectively (Table 1). Fig. 4 depicts the energy levels of PFTV, PFO, and PEDOT:PSS. Clearly the HOMO level of PFTV (-5.27 eV) situates between those of PEDOT:PSS $(-5.0 \sim -5.2 \text{ eV})$ [45] and PFO (-5.70 eV) [40], forming a stepwise energy ladder of HOMO levels to facilitate hole-injection. This means that the holeinjection from PEDOT:PSS to PFTV then transport to PFO is much easier than direct injection from PEDOT:PSS to PFO. Therefore, the improvement in hole-injection and transport are expected to enhance device efficiency.



Fig. 3. The AFM images of PFTV films coated on ITO glass: (a) pristine film, average rms roughness = 0.94 nm; (b) film thermally treated at 230 °C for 30 min, average rms roughness = 0.85 nm.



Fig. 5. Brightness versus bias and current density versus bias characteristics of multilayer PLEDs. Device structure: ITO/PEDOT:PSS/(PFTV)/PFO/LiF/Ca/Al. The PFTV film was cross-linked at 230 $^{\circ}$ C for 30 min.

3.4. Optoelectronic properties of multilayer PLEDs using **PFTV** as hole-transport layer

To evaluate the applicability of **PFTV** as hole-transporting layer for multilayer devices, a polymer light-emitting diode [ITO/ PEDOT:PSS/PFTV/PFO/LiF(1 nm)/Ca(50 nm)/Al(100 nm)] was fabricated by successive spin-coating process. The PFTV was spincoated on top of the PEDOT:PSS layer and treated at 230 °C for 30 min under nitrogen atmosphere, followed by the spin-coating of PFO solution. The PFO and LiF were used as emitting layer and electroninjection layer, respectively. The device without hole-transporting layer (ITO/PEDOT:PSS/PFO/LiF/Ca/Al) was also fabricated simultaneously for comparative study. Fig. 5 shows the current density versus bias and brightness versus bias curves (I-V-B) of the devices, with the characteristic data summarized in Table 2. The maximum brightness and maximum current efficiency of the device with cured **PFTV** as HTL are 4870 cd/m² and 1.15 cd/A, respectively. These performances are much better than those of the devices using pristine **PFTV** as HTL (2560 cd/m², 0.49 cd/A) or without **PFTV** layer $(2410 \text{ cd/m}^2, 0.50 \text{ cd/A})$. The result indicates that uncross-linked **PFTV** (pristine) contributes little in promoting the performance when compared with the device without PFTV as HTL. This is due to substantial dissolution of PFTV film during spin-coating of the emitting **PFO** layer. However, when thermally cross-linked **PFTV** is used as hole-transporting layer, both current efficiency and brightness are greatly enhanced (about 2 times). The enhancement is attributable to improved hole-injection from PEDOT:PSS to PFTV layers, which is much easier than direct injection from PEDOT:PSS to PFO layers. As mentioned above, the HOMO level of PFTV forms a stepwise energy ladder with those of PEDOT:PSS and PFO to facilitate hole-injection. To confirm hole-injection property of the

Table 2	
Optoelectronic properties of the multilayer PLEDs. ^a	

HTL	$V_{on}{}^{b}(V)$	L_{max}^{c} (cd/m ²)	$LE_{max} \left(cd/A \right)^d$	CIE 1931 (x, y) ^e
None	5.1	2410	0.50	(0.16, 0.08)
PFTV (cured) ^f	5.6	4870	1.15	(0.17, 0.08)
PFTV (uncured)	5.7	2560	0.49	(0.17, 0.10)
$\mathbf{PFTV} + DCP (cured)^{f}$	6.1	5560	2.27	(0.17, 0.10)

^a Device structure: ITO/PEDOT:PSS/HTL/**PFO**/LiF/Ca/Al; HTL: hole-transporting layer.

^b Turn-on voltage defined as the bias at a luminance of 10 cd/m².

^c Maximum luminance.
 ^d Maximum luminance efficiency.

^e The 1931 CIE coordinates at *ca*. 1000 cd/m².

^f Treated at 230 °C for 30 min.



Fig. 6. Emission spectra of light-emitting diodes using **PFO** or cross-linked **PFTV** as emitting layer. Device structures: (–) ITO/PEDOT:PSS/**PFO**/LiF/Ca/AI; (––) ITO/PEDOT:PSS/cross-linked **PFTV**(HTL)/**PFO**/LiF/Ca/AI; (–•–•) ITO/PEDOT:PSS/cross-linked **PFTV**/LiF/Ca/AI.

cross-linked **PFTV**, hole-only devices [ITO/PEDOT:PSS/with or without **PFTV/PFO**/Au(50 nm)/Al(100 nm)] were fabricated to investigate their current density versus electric field characteristics. Inserting a cross-linked **PFTV** layer shifts the curve to the left greatly, indicating that the cross-linked **PFTV** layer effectively increases the device's current density under the same external field (Fig. S2).

The EL spectra of the multilayer devices reveal similar emission peaks at 437 nm corresponding to $S_{10} \rightarrow S_{00}$ vibronic transition of fluorene segments (Fig. 6). To verify the EL emission is mainly contributed from emitting **PFO** layer, the device [ITO/PEDOT:PSS/ **PFTV**/LiF/Ca/Al] using cross-linked **PFTV** as emitting layer was fabricated to investigate its EL spectrum. The EL spectrum of using **PFTV** as emitting layer device shows a main peak at 479 nm and a shoulder at 444 nm, which are very different from that of multilayer devices. This indicates that the electrons and holes recombine mainly in the emitting **PFO** layer.

As mentioned previously, the degree of cross-linking can be increased by adding suitable cross-linking agents. The hole-transporting **PFTV** was thermally cured in the presence of dicumyl peroxide (DCP: 1 wt%) during the fabrication of a multilayer device [ITO/PDEOT:PSS/PFTV+DCP/PFO/LiF(1 nm)/Ca(50 nm)/Al(100 nm)]. The maximum brightness and maximum current efficiency are 5560 cd/m² and 2.27 cd/A (Table 2), respectively, which are higher than those without adding DCP (4870 cd/m^2 , 1.15 cd/A). The results demonstrate that increasing cross-linking density in **PFTV** layer gives rise to improved device performance. To conclude, the performance enhancement of the EL devices using PFTV as hole-transporting layer is attributed to promoted hole-injection ability. However, the **PFTV** layer should be thermally cross-linked during the fabrication processes to fully display its hole-transporting function. The **PFTV** is a promising hole-transporting material which can be employed in the fabrication of multilayer devices by successive spin-coating processes.

3.5. Optoelectronic properties of electrophosphorescent devices using **PFTV** as host

The efficacy of **PFTV** as an efficient hole-transporting material has been verified in multilayer PLEDs mentioned above. The **PFTV** seems applicable as host for electrophosphorescent devices because it contains triphenylamine moieties in main chain. However, the triplet energy (E_T) of the host should be larger than



Fig. 7. Absorption spectrum of $lr(piq)_2acac$ and PL spectrum of **PFTV** film coated on quartz plate (with λ_{ex} = 385 nm).

that of phosphorescent emitter to improve the efficiency of triplet-triplet energy transfer [46-48]. Therefore, phosphorescent emission spectrum of PFTV at 77 K in a frozen solution of toluene was measured to estimate its triplet energy. The phosphorescent emission maximum of PFTV is 559 nm, which corresponds to a triplet energy gap of 2.21 eV. This E_T of **PFTV** is higher than that of red-emitting dopant Ir(piq)₂acac (2.0 eV) [49], ensuring that the back energy transfer from Ir(piq)₂acac to **PFTV** can be effectively suppressed. Moreover, the PL spectrum of **PFTV** overlaps with that of Ir(piq)₂acac (Fig. 7), suggesting that efficient energy transfer from **PFTV** to Ir(piq)₂acac can be expected. As shown in Fig. 8, the PL intensity of **PFTV** doped with Ir(piq)₂acac decreases gradually with increasing weight percent of the dopant (from 2 wt% to 8 wt%). The emission spectra show two peaks at 442 and 620 nm, which originate respectively from PFTV host (PL) and Ir(piq)₂acac dopant (radiative decay from triplet state to ground state) [14]. The efficient energy transfer from host to dopant and suppressed back energy transfer are prerequisites for attaining high performance in host-guest electrophosphorescent devices.

Therefore, a series of EL devices, ITO/PEDOT:PSS/**PFTV**:Ir (piq)₂acac(110 nm)/Ca(50 nm)/Al (100 nm), using blends of **PFTV**



Fig. 8. PL spectra of the **PFTV** films doped with different amounts of $Ir(piq)_2acac$ (with $\lambda_{ex} = 385$ nm). The number represents weight percent of the $Ir(piq)_2acac$ in the film.



Fig. 9. EL spectra of the **PFTV** films doped with different amounts of lr(piq)₂acac. The number represents weight percent of the lr(piq)₂acac in the film.

and $Ir(piq)_2acac$ (2–8 wt%) as emitting layer were fabricated to investigate their optoelectronic characteristics. The main EL emission peak is around 620 nm with degenerated **PFTV** emission (400–530 nm). The EL emission of **PFTV** is almost completely



Fig. 10. Current density versus bias and brightness versus bias characteristics of PLEDs using Ir(piq)₂acac-doped **PFTV** as emitting layer. The number represents weight percent of the Ir(piq)₂acac in the film; devices structure: ITO/PEDOT:PSS/**PFTV**: Ir(piq)₂acac/Ca(50 nm)/Al(100 nm).

Table 5							
Optoelectronic pr	operties o	of the	electrophodphorescent	devices	using	PFTV	as
a host polymer do	ped with	Ir(piq)	₂ acac.				

Host ^a	$V_{on}^{c}(V)$	L_{max}^{d} (cd/m ²)	$LE_{max} (cd/A)^e$	CIE 1931 (x, y) ^f
PFTV2 ^b	6.1	4880	0.83	(0.58, 0.30)
PFTV4	6.7	5580	2.15	(0.64, 0.32)
PFTV8	7.1	4890	0.65	(0.66, 0.32)
PFTV4 ^g	6.7	5300	2.64	(0.65, 0.32)

^a Device structure: ITO/PEDOT:PSS/**PFTV**:Ir(piq)₂acac/Ca/Al.

^b The number presents weight percent of Ir(piq)₂acac in the film.

 $^{\rm c}$ Turn-on voltage defined as the bias at a luminance of 10 cd/m².

^d Maximum luminance.

^e Maximum luminance efficiency.

^f The 1931 CIE coordinates at *ca*. 1000 cd/m².

^g Device with additional LiF as electron-injection layer: ITO/PEDOT:PSS/**PFTV**: Ir(piq)₂acac/LiF/Ca/Al.

quenched at 4 wt% and 8 wt% Ir(pig)₂acac. The EL spectra peaked at 622 nm are similar to the PL spectrum of Ir(pig)₂acac (Fig. 8), indicating that the same emitting species are involved in both conditions. However, the EL emission spectra (Fig. 9) are very different from corresponding PL spectra (Fig. 8). This is presumably attributed to different underlying energy transfer mechanisms occurred under photo- and electro-excitation. The energy transfer from **PFTV** to Ir(pig)₂acac is more complete under electro-excitation which usually results in about 75% triplet excitons. Moreover, the Ir(piq)₂acac may act as carriers trapping sites due to its low band gap. Fig. 10 shows the current density versus bias and brightness versus bias curves (J-V-B), with the characteristic data summarized in Table 3. The maximum brightness and maximum current efficiency of the devices are 4880-5580 cd/m² and 0.65–2.15 cd/A, respectively. The turn-on voltage is increases from 6.1 V to 7.1 V with the increase of Ir(piq)₂acac concentration (2 wt% to 8 wt%), confirming that the Ir(piq)₂acac acts as charges trapping sites under electro-excitation. Because the HOMO (-5.17 eV) and LUMO (-3.23 eV) levels of Ir(piq)₂acac [33,49] lie between those of **PFTV** (-5.27 eV, -2.41 eV), both holes and electrons are readily trapped and recombined in Ir(piq)₂acac (Fig. 10).

The **PFTV4**-based device exhibits the best performance, with the maximum brightness and maximum current efficiency being 5580 cd/m² and 2.15 cd/A, respectively. With increasing $Ir(piq)_{2a}$ cac concentration the maximum current efficiency is first enhanced from 0.83 cd/A (2 wt%) to 2.15 cd/A (4 wt%) and then dropped abruptly to 0.65 cd/A (8 wt%). The abrupt reduction in efficiency at 8 wt% Ir(pig)₂acac is probably due to concentration guenching. In order to improve the EL performance, a device with extra lithium fluoride (LiF) layer was fabricated to balance charges injection and transport; the device structure was ITO/PEDOT:PSS/PFTV4 (110 nm)/LiF(1 nm)/Ca(50 nm)/Al(100 nm). Its maximum brightness and maximum current efficiency were 5300 cd/m^2 and 2.64 cd/A, respectively (Table 3). This efficiency enhancement (from 2.15 to 2.64 cd/A) is attributed to improved electron-injection by LiF layer that results in more balanced charges injection and transport. Current results demonstrate that **PFTV** is not only an efficient holetransporting polymer for electroluminescent devices but also applicable as host for electrophosphorescent devices.

4. Conclusions

We have successfully synthesized and characterized a thermally cross-linkable poly(fluorene-*co*-triphenylamine) (**PFTV**) containing pendent styryl groups by the Suzuki coupling reaction, which was applied as hole-transporting layer or as host in the fabrication of PLEDs. The **PFTV** demonstrated high thermal stability, with thermal decomposition (T_d) and glass transition (T_g) temperatures being

above 419 and 225 °C, respectively. Thermal curing of PFTV at 230 °C for 30 min led to homogeneous surface morphology with the root-mean-square (rms) roughness being 0.88 nm. The HOMO level of PFTV (-5.27 eV) lies between those of PEDOT:PSS $(-5.0 \sim -5.2 \text{ eV})$ and **PFO** (-5.8 eV), forming a stepwise energy ladder to facilitate hole-injection. The multilaver devices using cross-linked **PFTV** as hole-transporting laver [ITO/PEDOT:PSS/ PFTV/PFO/Ca/Al] were readily fabricated by successive spincoating processes. The device performances were significantly enhanced, by using the cured **PFTV** as hole-transporting layer. The best maximum current efficiency and brightness were 5560 cd/m² and 2.27 cd/A, respectively. Moreover, the PFTV was confirmed as effective host for electrophosphorescent devices with Ir(piq)₂acac as red emitter. The maximum brightness and maximum current efficiency reached 5300 cd/m² and 2.64 cd/A, respectively. Current results reveal that the **PFTV** is a promising optoelectronic material which is applicable not only as hole-transporting polymer in multilayer PLEDs but also as host polymer for electrophosphorescent LEDs.

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Appendix. Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.10.065.

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Table 2

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