



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 $\text{Ir}(\text{pic})_2\text{acac}$ to obtain a device with moderate performance (5300 cd/m^2 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 electroluminescence 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 ($E_{\text{HOMO}} = -5.8$ 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 spin-coating of the emitting layer.

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In the present study we synthesized a new thermally cross-linkable hole-transporting poly(fluorene-co-triphenylamine) (**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 cross-linking 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 (piq)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,N*-bis(4-bromophenyl)aniline (**5**) [38,39] were synthesized according to the procedures reported previously. 9,9-diarylfuorene-2,7-diboronic 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 Heraeus 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}): ν 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-, *J*₁ = 16 Hz, *J*₂ = 16 Hz), 5.80–5.76 (d, 1H, =CH₂, *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 ANAL. 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-diarylfuorene-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 light-yellow 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, -OCH₂-, *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,

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