# Synthesis of novel triphenylamine-based conjugated polyelectrolytes and their application as hole-transport layers in polymeric light-emitting diodes

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Received 13th March 2006, Accepted 11th April 2006 First published as an Advance Article on the web 5th May 2006 DOI: 10.1039/b603704f

Alternating triphenylamine-based copolymers poly[N-(4-sulfonatobutyloxyphenyl)-4,4'-diphenylamine-alt-1,4-phenylene] sodium salt (PTPOBS) and poly[N-(4-sulfonatophenyl)-4,4'-diphenylamine-alt-N-(p-trifluoromethyl)phenyl-4,4'-diphenylamine] sodium salt (PTFTS) were synthesized *via* palladium-catalyzed Suzuki coupling reaction. These polymers are soluble only in polar solvents, such as dimethyl sulfoxide (DMSO) and a mixed solvent of methanol and N,N-dimethyl formamide (DMF), rather than in non-polar solvents such as toluene and xylene. The electrochemical and photophysical properties of the resulted copolymers were investigated. The HOMO levels of the polymers (-5.08 eV for PTPOBS and -5.24 eV for PTFTS) were close to the work function of PEDOT. The relatively high-lying LUMO levels (-2.21 eV for PTPOBS and -2.24 eV for PTFTS) revealed that they had good electron-blocking capabilities. Devices with a PTPOBS or PTFTS layer inserted between ITO or PEDOT and of red and green-emitting polymers showed lower turn-on voltages and enhanced efficiency compared with the reference devices composed of bare ITO or ITO/PEDOT as anode. These polymers can be used as an independent hole-transport/electron-blocking layer or in combination with a PEDOT layer for fabrication of multilayer devices without intermixing with the subsequent EL layer by solution processing in full-color display applications.

# Introduction

Organic light-emitting diodes (OLEDs) are generally fabricated from ether small molecules,<sup>1-3</sup> dendrimers<sup>4</sup> or conjugated polymers.<sup>5</sup> Generally, OLEDs are thin-film multilayer structures composed of a hole-transporting, an emitting, and an electron-transporting layer sandwiched between two electrodes. Charge carriers (holes and electrons) are injected and transported from the anode and cathode, and are recombined in the emitting layer to emit light.<sup>6</sup> It is highly desirable to develop a suitable hole-transporting material (HTM) that possesses good mechanical, thermal and electrochemical properties. The HTM facilitates the hole injection and transport from the anode and also in many cases serve as an electron-blocking layer which blocks the electron movement to the anode and confine excitons within the emissive layer.<sup>1,7</sup> Triarylamine (TAA) derivatives, small molecules<sup>8</sup> or polymers with a TAA unit in the polymer backbone<sup>9a-c</sup> or in pendant<sup>9d-f</sup> groups, are one of the most widely-used holetransporting materials because they are easily oxidized to form stable radical cations.10

Polymer light-emitting diodes (PLEDs) have recently attracted researchers' intense interest due to their possible applications in large-area flat panel displays based on solution printing techniques. The advantage of OLEDs with multilayer device configuration, typically fabricated by thermal deposition, over polymer light-emitting devices (PLEDs) with typical

single-layer device configuration is that OLEDs with multiple layer structures allow the recombination zone to be confined in a very narrow emission layer between the hole-transport (electron-blocking) and electron-transport (hole-blocking) layers. A challenge to the fabrication of multilayer devices via solution processing is that the application of subsequent layers may result in the erosion of the layers that have been applied in the previous steps. One of the solutions to the fabrication of erosion-resistant HTLs is to make such materials insoluble by thermal or photochemical crosslinking prior to the processing of the emitting layer. Varieties of photo-crosslinkable<sup>11</sup> and thermally crosslinkable<sup>12</sup> HTMs have been synthesized recently. An alternative solution is to use HTMs which are processable in solvents in which emitting polymers are not soluble. A typical example is the widely-used anode buffer PEDOT-PSS,<sup>13</sup> which is a microemulsion in water. Recently, Gong et al.<sup>14</sup> reported ethanol-soluble, sulfonated poly(N-vinylcarbazole) (PVK) and PVK-SO<sub>3</sub>Li,<sup>15</sup> which can be used as the hole-transport layer in a multilayer white-light emission PLED.

In this paper, we report the synthesis of two sulfonate substituted polytriphenylamine polyelectrolytes, which are soluble only in polar solvents. The redox potentials of the two polymers can be adjusted by the attachment of electron-donating (butyloxy) or electron-withdrawing  $(-CF_3, -SO_3^-)$  groups to the main chain. Excellent hole-transporting and electron-blocking properties in combination with good solubility in polar solvents make them promising candidates for hole transport layers in the fabrication of high-efficiency multilayer polymer light-emitting devices and displays.

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## Experimental

## 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. All the solvents used were further purified before use. N,N-Di-p-bromophenyl-(p-trifluoromethyl)aniline,<sup>16</sup> N,Nbis(4-bromophenyl)aniline<sup>17</sup> and poly(9,9-dioctylfluorene-co-4,7-dithien-2-yl-2,1,3-benzothiadiazole (PFO-DBT15)<sup>18</sup> were prepared according to the published procedures. Poly(9,9dioctylfluorene-co-2,1,3-benzothiadiazole) (PFO-BT15) was synthesized using a procedure similar to that described in the literature.<sup>12b</sup>

4-Methoxy-*N*,*N*-bis(4-bromophenyl)aniline (1). Toluene (50 ml), 4-methoxyaniline (6.16 g, 50.0 mmol), 1-bromo-4iodobenzene (31.8 g, 110.0 mmol), phenanthroline (0.337 g, 1.87 mmol), cuprous chloride (CuCl) (0.196 g, 1.87 mmol) and potassium hydroxide (KOH) (flakes, 86%, 26.8 g, 391 mmol) were added sequentially to a 250 ml three-necked flask equipped with condenser, magnetic stirrer, nitrogen inlet and outlet under nitrogen. The reaction mixture was heated to reflux in 30 min and was stirred at reflux for 48 h. Then the mixture was cooled to 75 °C, 150 ml of toluene and 100 ml of distilled water were used in extraction. The toluene phase was separated, dried with anhydrous magnesium sulfate (MgSO<sub>4</sub>), filtered and vacuum distilled. The crude product was purified by silica column chromatography using petroleum ether-ethyl acetate (19 : 1 v/v) as eluent to give 1 (8 g. 37%) as a colorless viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.34– 7.31 (d, 4H, aromatic H), 7.07-7.04 (d, 2H, aromatic H), 6.93-6.90 (d, 4H, aromatic H), 6.89-6.86 (d, 2H, aromatic H), 3.83 (s, 3H,  $-OCH_3$ ), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 156.75, 146.83, 139.74, 132.17, 127.41, 124.48, 115.04, 114.56, 55.50 (-OCH<sub>3</sub>).

4-Hydroxy-N,N-bis(4-bromophenyl)aniline (2). A solution of boron tribromide (BBr<sub>3</sub>) (1.75 ml, 18.5 mmol) in 18.5 ml of dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was added dropwise to a solution of 1 (5.3 g, 12.2 mmol) in 90 ml of dry CH<sub>2</sub>Cl<sub>2</sub> at room temperature. After being stirred at room temperature overnight, the mixture was slowly poured into 250 ml of distilled water and stirred for another hour. The organic phase was separated and the water phase was extracted by CH<sub>2</sub>Cl<sub>2</sub> until colorless. The organic phase was combined and dried over MgSO<sub>4</sub>. Column chromatography using silica gel and petroleum ether– $CH_2Cl_2$  (1 : 3 v/v) as eluent to afford 2 (4.5 g, 88%) as pale green solids. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.34-7.31 (d, 4H, aromatic H), 7.01-6.98 (d, 2H, aromatic H), 6.92-6.89 (d, 4H, aromatic H), 6.82-6.79 (d, 2H, aromatic H), 5.25 (s, 1H, –OH), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 152.69, 146.80, 139.89, 132.19 127.61, 124.30, 116.57, 114.61.

**4-***N*,*N*-**Bis(4-bromophenyl)amino-1-(sulfonatobutyloxy)benzene sodium salt (3).** Added into a 100 ml three-necked roundbottomed flask were **2** (2.0 g, 4.8 mmol) and sodium methoxide (0.38 g, 7 mmol) under nitrogen and then 45 ml of absolute ethanol was added. After this mixture was refluxed for 1 h, 1,4butanesulfonate (0.82 g, 6.0 mmol) was added *via* syringe. The mixture was stirred at reflux in a nitrogen flow for 24 h. The product precipitated after being cooled to room temperature. The filtrate was recrystallized from absolute ethanol to give a white powder (1.6 g, 58%). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ (ppm): 7.44–7.38 (d, 4H, aromatic H), 7.03–7.01 (d, 2H, aromatic H), 6.95–6.92 (d, 2H, aromatic H), 6.89–6.86 (d, 4H, aromatic H), 3.94–3.92 (t, 2H,  $-\text{OCH}_2-$ ), 2.46–2.45 (t, 2H,  $-\text{CH}_2\text{SO}_3\text{Na}$ ), 1.77–1.70 (m, 4H,  $-\text{CH}_2-\text{CH}_2-$ ), <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>) δ (ppm): 156.75, 147.13, 139.27, 132.75, 128.34, 124.63, 116.38, 114.24, 68.14, 51.64, 28.61, 22.48. Elem. Anal. Calcd for C<sub>22</sub>H<sub>20</sub>Br<sub>2</sub>NO<sub>4</sub>SNa·1.0H<sub>2</sub>O: C, 44.37; H, 3.70; N, 2.35; S, 5.38. Found: C, 44.40; H, 3.70; N, 2.06; S, 6.09%.

4-(N,N-Bis(4-bromophenyl)amino)benzene sulfonic sodium salt (4). N.N-Bis(4-bromophenyl)aniline (2.27 g, 5.63 mmol) was dissolved in 35 ml of dichloromethane. Added dropwise to this solution was chlorosulfonic acid (0.5 ml, 7.319 mmol) at room temperature. The reaction mixture was stirred at a room temperature for 1 h and then was poured into crushed ice. 50%NaOH (aq) was added to this mixture until pH > 9. The precipitate was filtered off and recrystallized from distilled water, then vacuum dried at 80 °C for 24 h to a give silvery white solid (1.51 g, 53%). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ (ppm): 7.51-7.49 (d, 2H, aromatic H), 7.44-7.40 (d, 4H, aromatic H), 6.93-6.91 (d, 2H, aromatic H), 6.92-6.89 (d, 4H, aromatic H),  ${}^{13}$ C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 146.93, 146.70, 144.44, 133.01, 127.83, 126.17, 123.82, 115.51. Elem. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>Br<sub>2</sub>NO<sub>3</sub>SNa·1.4H<sub>2</sub>O: C, 40.74; H, 2.79; N, 2.64; S, 6.04. Found: C, 40.98; H, 2.80; N, 2.46; S, 6.43%.

N,N-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-(p-trifluoromethyl)aniline (5). In a 250 ml three-necked flask in an argon flow, N,N-di-p-bromophenyl-(p-trifluoromethyl)aniline (9.0 g, 19.05 mmol) was dissolved in 120 ml of anhydrous tetrahydrofuran (THF). The solution was cooled to -78 °C, and then n-butyllithium solution (n-BuLi) (1.6 M in hexane, 25 ml, 40 mmol) was slowly added. The reaction mixture was stirred at this temperature for 2 h. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30 ml, 128.6 mmol) was quickly added via syringe. The resulting mixture was stirred at -78 °C for 2 h, and then was slowly warmed to room temperature and stirring continued for 48 h. Distilled water (50 ml) was added to the reaction mixture which was extracted using dichloromethane (3  $\times$  100 mL). The organic phase was separated and dried over MgSO<sub>4</sub> overnight. The solvent was distilled, and the crude product was purified by recrystallization from hexane-ethyl acetate (19 : 1 v/v) to give a white solid (5.7 g, 53%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.76–7.73 (d, 4H, aromatic H), 7.48-7.45 (d, 2H, aromatic H), 7.15-7.12 (d, 2H, aromatic ring), 7.12–7.09 (d, 4H, aromatic H), 1.36 (s, 24H, –CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 150.23, 149.31, 136.14, 126.39, 126.34, 126.07, 124.19, 123.92, 123.00, 83.78, 24.87.

Poly[*N*-(4-sulfonatobutyloxyphenyl)-4,4'-diphenylamine-alt-1,4-phenylene] sodium salt (PTPOBS). Added into a 250 ml three-necked flask was 4-N,N-bis(4-bromophenyl)amino-1-(sulfonatobutyloxy)benzene sodium salt (3) (0.866 g, 1.5 mmol), 1,4-phenyldiboronic acid (0.249 g, 1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (1.5 g, 14.2 mmol) and Pd(OAc)<sub>2</sub> (palladium acetate) (0.010 g, 3 mol%) under nitrogen. The content was purged with nitrogen for 30 min, then 70 ml of distilled water and 30 ml of DMF were injected by syringe after 1 hour deaeration. The reaction mixture was heated to 85-90 °C and stirred for 48 h. After being cooled to room temperature, the mixture was poured into 1 L of acetone. The precipitate was collected and redissolved into a minimum amount of DMSO, filtered off and dialyzed using a membrane with an 8000 molecular weight cutoff for 3 days. Water was vacuum distilled and the final product was obtained after drying in vacuum at 80 °C for 24 h (0.25 g, 40%). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 7.70– 7.64 (m, 8H, aromatic H), 7.08-6.98 (m, 8H, aromatic H), 3.97 (m, 2H, -OCH<sub>2</sub>-), 2.50 (m, 2H, -CH<sub>2</sub>SO<sub>3</sub>Na), 1.77-1.70 (m, 4H,  $-CH_2-CH_2-$ ), <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 156.50, 147.40, 139.84, 138.55, 133.52, 128.37, 127.94, 127.11, 123.09, 116.29, 68.14, 51.69, 28.66, 22.50. Elem. Anal. Calcd for C<sub>28</sub>H<sub>24</sub>NO<sub>4</sub>SNa·0.8H<sub>2</sub>O: C, 66.22; H, 5.05; N, 2.76; S, 6.31. Found: C, 65.00; H, 6.08; N, 3.45; S, 6.10%.

Poly[N-(4-sulfonatophenyl)-4,4'-diphenylamine-alt-N-(p-trifluoromethyl)phenyl-4,4'-diphenylaminel sodium salt (PTFTS). Added into a 250 ml three-necked flask were 4-(N,N-bis(4bromophenyl)amino)benzene sulfonic sodium salt (4) (1.01 g, 2.0 mmol), N,N-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-(p-trifluoromethyl)aniline (5) (1.132 g, 2.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.0 g, 18.9 mmol), 95 ml of distilled water, 40 ml of DMF and 25 ml of THF. Into the mixture was added Pd(OAc)<sub>2</sub> (0.014 g, 3 mol%) after being purged with nitrogen for 30 min. The reaction was carried out at 85-90 °C and vigorously stirred for 24 h. The second portion (0.014 g) of Pd(OAc)<sub>2</sub> was added and stirring continued at 85–90 °C for another 24 h. After being cooled to room temperature, the mixture was poured into 1 L of acetone. The precipitate was collected and redissolved into a minimum amount of DMSO. filtered off and dialyzed using a membrane with an 8000 molecular weight cutoff for 3 days. Water was vacuum distilled and the final product was obtained after drying in vacuo at 80 °C for 24 h (1.25 g, 40%). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ (ppm): 7.65-7.56 (m, 12H, aromatic H), 7.22-7.02 (m 12H, aromatic H), <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 151.01, 147.36, 146.62, 145.40, 143.71, 136.20, 134.40, 128.15, 128.00, 127.59, 127.09, 126.18, 124.48, 123.53, 123.26, 121.84, 121.20. Elem. Anal. Calcd for C<sub>37</sub>H<sub>24</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SNa·1.3H<sub>2</sub>O: C, 65.35; H, 3.92; N, 4.12; S, 4.71. Found: C, 64.19; H, 4.82; N, 4.12; S, 5.05%.

## Chemical characterization

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a Bruker DRX 300 spectrometer operating at 300 MHz (for <sup>1</sup>H) and 75 MHz (for <sup>13</sup>C), in deuterated chloroform or DMSO solution with tetramethylsilane as reference. Number-average  $(M_n)$  and weight-average  $(M_w)$  molecular weights were determined by multi-angle laser light scattering combined with size exclusion chromatography (MALLS-SEC), which was

performed with a multi-angle photometer (DAWN-DSP, Wyatt Technology Co.) at 633 nm and at 25 °C with DMSO eluent at a flow rate of 1.0 ml min<sup>-1</sup>. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). UV-visible absorption spectra were recorded on a HP 8453 UV-Vis spectrophotometer. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s<sup>-1</sup> against a saturated calomel reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile (CH<sub>3</sub>CN). Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 at a heating rate of 10 °C min<sup>-1</sup> and a nitrogen flow rate of 20 mL min<sup>-1</sup>.

## LED fabrication and characterization

PLEDs with the triphenylamine-based polyelectrolytes as HTL were investigated. The device structures were ITO/(PEDOT)/ HTL/emissive polymer/Ba/Al. Patterned indium tin oxide (ITO) coated glass substrates were cleaned with acetone, detergent, distilled water and isopropanol in an ultrasonic bath, and were treated with oxygen plasma before use. If necessary, an 80 nm layer of PEDOT was spin-coated on the cleaned ITO from an aq. emulsion of PEDOT : PSS (Baytron P, Bayer A.G.) [poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS)] followed by drying in a vacuum oven at 80 °C for 8 h. About 1 wt% of hole-transport materials PTPOBS and PTFTS were dissolved in the mixed solvent of methanol and DMF (CH<sub>3</sub>OH : DMF = 4 : 1 v/v), filtered through a 0.45 µm filter and spin-coated on top of ITO or PEDOT inside a dry box. The film thicknesses of the polyelectrolytes were around 40 nm, as measured with a Tencor Alfa step 500 surface profiler. Emissive poly(9,9-dioctylfluorene-co-4,7-dithien-2-yl-2,1,3material benzothiadiazole) (PFO-DBT15, DOF : DBT = 85 : 15) and poly(9,9-dioctylfluorene-co-2,1,3-benzothiadiazole) (PFO-BT15, DOF : BT = 85:15) were dissolved in toluene, filtered through a 0.45 µm filter and spin-coated onto the anode to form a film of about 80 nm. Ba and Al layers were vacuumevaporated on the top of an EL polymer in a vacuum of  $1 \times$  $10^{-4}$  Pa. To reveal the hole-transport effect caused by these two polyelectrolytes, devices without HTL having structures ITO/emissive polymer (80 nm)/Ba/Al, and ITO/PEDOT : PSS (80 nm)/emissive polymer (80 nm)/Ba/Al were made as references. The current density-voltage-luminance (J-V-L) characteristics were measured by a Keithley 236 sourcemeasurement unit and a calibrated silicon photodiode which was calibrated for luminance by a PR-705 SpectraScan Spectrophotometer (Photo Research). The external EL quantum efficiency (QE) was collected by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere).

## **Results and discussion**

## Synthesis and characterization

The synthesis route is shown in Scheme 1. Compound  ${\bf 1}$  was synthesized by the improved Ullmann reaction using the



Scheme 1 Synthesis route of the monomers and polymers and chemical structure of PLED emissive layers, PFO-DBT15 and PFO-BT15.

catalyst system composed of phenanthroline, CuCl and KOH, which was used to synthesize triphenylamine derivatives according to Goodbrand and Hu.<sup>19</sup> By the treatment of **1** with BBr<sub>3</sub> in dry dichloromethane, **2** was obtained as pale green solid in 88% yield after column chromatography using silica gel and petroleum ether–CH<sub>2</sub>Cl<sub>2</sub> (1 : 3 v/v) as eluent. Compound **2** was alkoxylated by 1,4-butanesulfonate in the presence of sodium methoxide in refluxing absolute ethanol to give monomer **3**. *N*,*N*-Bis(4-bromophenyl)aniline reacted with chlorosulfonic acid in CH<sub>2</sub>Cl<sub>2</sub> at a room temperature, and was then neutralized by aqueous NaOH to give monomer 4. Several attempts to induce sulfonic groups by using conc.  $H_2SO_4$  (98%) were unsuccessful. Due to the existence of the sulfonate group in the side chain, monomers 3 and 4 are not soluble in most common organic non-polar solvents, such as chloroform, toluene and xylene, but are soluble in polar solvents, such as water, DMF and DMSO. *N*,*N*-Di-*p*-bromophenyl-(*p*-trifluoromethyl)aniline was first lithiated by *n*-BuLi in dry THF and then reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give the boronic acid ester substituted product 5 in 53% yield.

The polymers were synthesized by Pd(OAc)<sub>2</sub>-catalyzed Suzuki cross-coupling polymerization as described by Child and Reynolds<sup>20</sup> and Kim et al.<sup>21</sup> for the preparation of poly(p-phenylene) analogues. A mixture of an 0.2 M aqueous solution of Na<sub>2</sub>CO<sub>3</sub> and DMF (70 : 30 v/v) was utilized as the polymerization medium. The reactions were conducted at 85-90 °C for 48 h. A difference in the synthesis of PTPOBS and PTFTS is that, since N,N-bis[4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)phenyl]-(p-trifluoromethyl)aniline (5) is not soluble in the reaction mixture, we added some THF to dissolve monomer 5 and make its hydrolysis faster. Another portion of Pd(OAc)<sub>2</sub> was added to complete the reaction in the synthesis of PTFTS, similar to what Balanda et al, described for the synthesis of cationic poly(p-phenylene).<sup>22</sup> The resulting polymers were precipitated in acetone after being cooled to room temperature. The precipitates were redissolved in DMSO and filtered to remove the Pd particles. The filtrate was dialyzed using a membrane with a cut-off of 8000 molecular weight for 3 days. In this process we changed fresh distilled water several times to remove DMSO, ionic impurities and low molecular weight oligomers. The final products were obtained by the evaporation of the water. The yield was about 40% after both polymers were dried in a vacuum oven at 80 °C. The obtained polymers PTPOBS and PTFTS were readily dissolved in DMSO and in a mixture of methanol-DMF, but they were insoluble in non-polar organic solvents, such as chloroform, toluene, xylene and chlorobenzene. As they can withstand the erosion of commonly-used non-polar organic solvents, these two polymers can efficiently avoid interface mixing when they are used as HTL during the fabrication of multilayer PLEDs. Multi-angle laser light scattering combined with size exclusion chromatography (MALLS-SEC) analysis<sup>23</sup> showed the average molecular weights of  $M_{\rm n}$  = 36 580 (±3%) and  $M_{\rm w} = 61\ 400\ (\pm 4\%)$  for PTPOBS,  $M_{\rm n} = 11\ 600\ (\pm 8\%)$ and  $M_{\rm w} = 26$ ,820 (±4%) for PTFTS.

The chemical structures of all the monomers and polymers were verified by <sup>1</sup>H, <sup>13</sup>C NMR and elemental analysis.

The thermal properties of these two polymers were investigated using thermogravimetric analysis (TGA). We note that there is always some water remaining in both polymers,<sup>24</sup> even if the polymers were dried for a long time in a vacuum at 100 °C. The amounts of water in the polymers were estimated at about 3% for both polymers by TGA. Fig. 1 shows the thermograms of these two polymers. The temperature ranges from 25 to 800 °C in a nitrogen atmosphere. There is a small amount of water loss at a lower temperature for both polymers.<sup>24</sup> The onset of degradation temperatures for PTPOBS and PTFTS are about 237 and 233 °C, which is associated with desulfonation.<sup>21</sup>

#### Optical and electrochemical properties

Transparent uniform films of the polymers were prepared on quartz substrates by spin-casting from a mixed solvent DMF– MeOH (1 : 4 v/v) solution of PTPOBS and PTFTS. Fig. 2 shows UV-visible absorption and PL spectra of the two polymers in the solid form under 325 nm excitation from a HeCd laser diode. Compared with PTPOBS, both the absorption and PL emission of PTFTS copolymer are significantly



Fig. 1 Thermogravimetric analysis of PTPOBS and PTFTS in a nitrogen atmosphere.

blue-shifted. The main absorption peaks of PTPOBS and PTFTS were 376 and 357 nm, respectively. The optical band gaps of the copolymers estimated from the onset of the UV-vis absorption band (432 nm for PTPOBS, 415 nm for PTFTS) are 2.87 and 2.99 eV, respectively. The two polymers emit blue light when excited by UV light. The PL spectra reached maxima at 450 nm for PTPOBS and at 425 nm for PTFTS. There are two possible explanations for the blue-shift of the absorption and PL spectra of PTFTS compared with PTPOBS. First, this shows that the conjugation length of the PTPOBS backbone is longer than that of PTFTS. For PTPOBS the triphenylamine groups are connected to the phenylene group alternately in the polymer backbone, which may result in a longer  $\pi$ -conjugation than PTFTS without phenylene moieties in the backbone. Then, two electronwithdrawing groups ( $-CF_3$  and  $-SO_3^-$ ) are directly connected to the polymer main chain, resulting in greater reduction of the electron density of the PTFTS backbone than that of PTPOBS.

The electrochemical behavior of the polymers was investigated by cyclic voltammetry (CV). The CV was performed in a solution of  $Bu_4NPF_6$  (0.1 M) in acetonitrile at a scan rate of 50 mV s<sup>-1</sup> at room temperature under argon. A platinum electrode was used as the working electrode, a Pt wire was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. As shown in Fig. 3, for



Fig. 2 UV-vis absorption and PL emission spectra of PTPOBS and PTFTS copolymers in solid-state films.



Fig. 3 Cyclic voltammograms of the polymer films coated on platinum electrodes in 0.1 mol  $L^{-1}$  Bu<sub>4</sub>NPF<sub>6</sub>, CH<sub>3</sub>CN solution.

PTPOBS the oxidative process started at around 0.68 V and gave a sharp oxidative peak at 1.10 V. The oxidation is reversible, and the corresponding deoxidation peak appears at 0.70 V. The CV behavior of PTPOBS, including the oxidation onset, oxidation and deoxidation peaks and CV curve profile, is very similar to that of poly[N-(4-butylphenyl)amino(1,1':4',1"-terphenyl-4',4"-ylene)] (PBPITP),<sup>9b</sup> which has a similar chemical structure to PTPOBS. Similar to PTPOBS, one oxidation peak was observed during the anodic scan of the PTFTS copolymer. The oxidation started at around 0.83 V with a peak around 1.40 V, highly reversible and was deoxidized at 0.70 V. The energy levels of the highest occupied molecular orbitals (HOMOs) of PTPOBS and PTFTS were estimated from the onset of the oxidation wave, calculated according to an empirical formula,  $E_{HOMO} = -e(E_{ox} +$ 4.4) (eV),<sup>25</sup> to be -5.08 and -5.23 eV, respectively. In the cathodic scan, no reduction peak (down to -2.5 V vs. SCE) was observed for both PTPOBS and PTFTS copolymers. The level of the lowest unoccupied molecular orbital (LUMO) can be estimated by subtracting the optical band gap energy from the HOMO, as determined by electrochemistry. The LUMO levels of PTPOBS and PTFTS were respectively estimated at -2.21 and -2.24 eV. The relatively high-lying LUMO levels reveal that it is difficult to inject electrons to these two polymers. In other words, they may serve as an electronblocking layer when they are inserted between an emission layer and an anode.

The UV-visible absorption, electrochemical and photoluminescence properties of these polymers in solid films are summarized in Table 1.

#### **Electroluminescence** properties

To verify the hole-injection and transport properties of these new hole-transport polymers, red (PFO-DBT15) and green



**Fig. 4** Energy-level diagram of PLED components; the band-edge energy levels were determined by CV or taken from the literature.



**Fig. 5** EL spectra of red and green emitting PLEDs with PTPOBS or PTFTS as HTL, structure ITO/(PEDOT : PSS)/(PTPOBS or PTFTS)/ PFO-DBT15 or PFO-BT15/Ba/Al.

(PFO-BT15) emitting polymers (see Scheme 1) were used to fabricate multilayer devices with PTPOBS and PTFTS as HTL on the top of bare ITO or PEDOT : PSS. Fig. 4 shows the energy-level diagram of different layers in the PLEDs composed of these materials.

Fig. 5 shows EL spectra of PFO-DBT15 and PFO-BT15 in different device configurations. The similar EL emission for both EL emitting polymers, regardless of HTL material used, indicates that the recombination zone is always confined in the emissive layer when PTPOBS and PTFTS are inserted between the emissive layer and anode.

Fig. 6a compares the external quantum efficiency of redemitting devices based on PFO-DBT15 with PTPOBS or PTFTS inserted between ITO or PEDOT and the emissive layer. Both PTPOBS and PTFTS enhance the device efficiency significantly compared with the devices only composed of ITO or PEDOT without HTL (PTPOBS or PTFTS). It is important to note that the efficiency of a device with PTPOBS and PTFTS as HTL on the top of ITO substrate without PEDOT layer is much higher than that of a device with the very well

 Table 1
 UV-Vis absorption, electrochemical, photoluminescence properties of the polymers (in solid films)

Polymers	$\lambda_{absn}$	<sub>nax</sub> /nm	Op	tical	ban	d gap <sup>a</sup> /eV	$V = E_{c}$	x/V	1	Еномо	/eV	$E_{\rm LUMC}$	<sup>b</sup> /eV		$\lambda_{PLmax}$	/nm	
PTPOBS PTFTS	376 357		2.8 2.9	7 9			0.0 0.3	58 33	-	-5.08 -5.23		$-2.21 \\ -2.24$			450 425		
<sup><i>a</i></sup> Estimated from optical band gate	p. the	onset	wavelength	of	the	optical	absorption	in th	e solid	state	film.	<sup>b</sup> Calculated	from	the	НОМО	level	and



Fig. 6 Device characteristics of the red-emitting PLEDs with structure ITO/(PEDOT)/(PTPOBS or PTFTS)/PFO-DBT15/Ba/Al. (a) External quantum efficiency-bias (V) characteristics. (b) Brightness-bias (V) characteristics.

investigated PEDOT layer, although their HOMO levels are close. This may be because the relatively high-lying LUMO levels of PTPOBS and PTFTS served as an electron-blocking layer. The LUMO energy gap between PFO-DBT15 and PTPOBS, PTFTS was about 1.3 eV; this energy barrier blocks the movement of electrons to the anode and confine electrons in the emissive layer. Consequently, the hole–electron recombination took place in a more balanced way in the emissive layer resulting in high efficiency (Fig. 6, 7). Since PEDOT has as LUMO of around 3.4 eV (Fig. 4), electrons can easily move from the emissive layer across the PEDOT layer reaching the anode.

Fig. 6b shows luminance vs. bias for the same devices as in Fig. 6a. The turn-on voltage (turn-on voltage is defined as the voltage required for a device to reach a luminance of  $\sim 1$  cd m<sup>-2</sup>) is 6.2 V for the device with bare ITO as anode. When a HTL was insert between ITO and the EML, the turnon voltage was reduced significantly to 4.4 V for PTPOBS and 3.2 V for PTFTS. We note that the turn-on voltage with PTFTS is also lower than that of the device with PEDOT (3.6 V) as anode buffer layer. The lower turn-on voltage is due to the reduced barrier height in the anode-EM polymer interface as a result of the insertion of PTPOBS or PTFTS layers. As can be seen from the energy-level diagram of PLED components shown in Fig. 4, the energy barrier for holes directly injected from ITO to the PFO-DBT15 emissive layer is about 0.8 eV. This relatively large energy level mismatch makes hole injection difficult. By the insertion of a holetransport layer, the hole injection barrier height was reduced and hence hole injection was enhanced. The best device performance was realized for a device with a PEDOT/PTFTS



Fig. 7 Device characteristics of the green-emitting PLEDs with structure ITO/(PEDOT)/(PTFTS)/PFO-BT15/Ba/Al. (a) External quantum efficiency-current density characteristics. (b) Brightness-current density characteristics.

layer as HTL, giving a saturated red emission with luminance of 2000 cd m<sup>-2</sup> at 7.6 V and CIE coordinate of (0.68, 0.31) with an external QE over 1%. In Table 2 we compare the device performance with different HTLs at a current density of around 33 mA cm<sup>-2</sup>.

Similar results were obtained for the green-emitting polymer, PFO-BT15, with PTFTS as HTL. Fig. 7a shows that a significant improvement in device efficiency can be observed for the device with a PTFTS layer on top of ITO or PEDOT, as in the case of red-emitting polymers. The device with

**Table 2** Device performance of the red-emitting (PFO-DBT15) devices at a current density of about 33 mA cm<sup>-2</sup>

	Device performance <sup>a</sup>							
Device structure	Bias/V	$I/mA \text{ cm}^{-2}$	Luminance/cd m <sup>-2</sup>	QE <sub>ext</sub> (%)				
PTPOBS	8.3	36.5	201	1.5				
PTFTS	6.9	33.7	176	1.4				
PEDOT/PTPOBS	7.9	33.1	165	1.3				
PEDOT/PTFTS	5.2	31.3	160	1.4				
Bare ITO	8.9	34.8	38	0.3				
PEDOT : PSS	5.4	37.3	124	0.9				
<sup><i>a</i></sup> Device active are	ea 0.15 c	$cm^2$ .						

Table 3 Device performance of the green-emitting (PFO-BT15) devices at a current density of about 33 mA  $\rm cm^{-2}$ 

	Device performance <sup>a</sup>							
Device structure	Bias/V	$I/mA \text{ cm}^{-2}$	Luminance/cd $m^{-2}$	QEext (%)				
PTFTS PEDOT/PTFTS Bare ITO PEDOT : PSS	9.4 7.5 9.2 5.9	35.3 32.2 34.1 38.4	1357 843 31 738	2.3 1.5 0.054 1.1				
<sup>a</sup> Device active a	rea 0.15	cm <sup>2</sup> .						

PTFTS alone on top of the ITO substrate exhibits the most impressive performance with a turn-on voltage of 3.7 V and luminance of 5150 cd m<sup>-2</sup> at a current density of 154 mA cm<sup>-2</sup>(Fig. 7b), the maximum EL quantum efficiency reaching 2.4% at 7.2 V. Table 3 summarizes the device performance of green-emitting polymers with different HTL layers at a current density of around 33 mA cm<sup>-2</sup>.

The results indicate that PTPOBS and PTFTS are excellent HTL materials, superior to PEDOT in PLED applications. These polymers can be used alone or in combination with a PEDOT layer for the fabrication of multilayer devices by using solution processing techniques in full-color display applications.

#### Conclusions

We have developed two conjugated polyelectrolytes based on triphenylamine, PTPOBS and PTFTS, through Suzuki coupling reaction. The low oxidation potentials and high-lying LUMO levels make these two polymers excellent hole-injecting and electron-blocking materials. These polymers are soluble only in polar solvents, rather than in non-polar solvents, in which most light-emitting polymers are processed. We have proved that, after inserting these two polymers between ITO or PEDOT and red light-emitting (PFO-DBT15) or greenemitting (PFO-BT15) layers, the devices showed lower turnon voltage, higher brightness and enhanced external quantum efficiencies compared with a single-layer device with bare ITO as anode or a device with PEDOT as HTL. Excellent holetransporting and electron-blocking properties together with good solubility in polar solvents make them promising candidates for hole transport layers in the fabrication of high-efficiency multilayer polymer light-emitting devices and displays by solution processing techniques.

## Acknowledgements

The authors greatly appreciate the financial support from the National Natural Science Foundation of China (Project No. 50433030) and the Ministry of Science and Technology, project no. 2002CB613402.

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